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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

April 1963

● VOLUME 6

● NUMBER 2

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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

Domestic Plans

Operators of licensed reactors have now been given the option, under certain conditions, of making deliveries of used reactor fuel to the Atomic Energy Commission (AEC) by transferring the spent nuclear fuel elements to AEC and storing them for AEC at the reactor sites.[1] Previously, only AEC processing plants at Idaho and Savannah River were designated as receiving sites for spent fuel elements. When delivery is made, whether at the reactor or at other AEC receiving sites, the reactor operator is required to make financial settlement with AEC, including its charges for chemical processing and conversion, in accordance with existing AEC policies. Operators of the Dresden and Yankee nuclear power stations have accepted the arrangement for storing spent fuel at the reactor sites. The first fuel discharge from these reactors are scheduled to be delivered to AEC this spring.

The reactor operators will also have the option, under terms to be negotiated, of arranging to have the stored fuel elements, previously transferred to AEC, processed by a private company that is licensed to perform the operation of recovering unburned fissionable material from such fuel elements. These options have been offered by AEC because private industry may construct a processing facility. Storage of spent fuel at the reactor sites would avoid reshipment of such fuel from the AEC site to a private facility.

At the end of 1962, completion of the AEC review of the Nuclear Fuel Services (NFS) processing charges had not yet been reported. Issuance of a construction permit would be expected to follow. In October 1962 AEC granted preliminary approval of the West Valley, N. Y., site. It has been reported that NFS has verbal commitments and letters of intent from the Dresden and Yankee reactor operators, stating that these utilities would process the first cores at the NFS plant if AEC approves the project.[2]

NFS has indicated to AEC that it plans to enter the field of processing and fabrication of fuels, as well as the processing of spent fuels. NFS is to acquire the nuclear materials processing plant of Davison Chemical Company at Erwin, Tenn., and also the Port Hope, Ontario, fuel-fabrication plant of American Machine & Foundary (AMF) Atomics of Canada, Ltd. AMF holds a 22% interest in NFS.[3]

Oak Ridge National Laboratory (ORNL) plans to start construction in 1963 of a thorium fuel-cycle development facility in which all phases of the thorium-U^{233} fuel cycle can be explored and developed to economic feasibility. The facility will be capable of processing and refabricating fuel elements as long as 12 ft in batches containing up to 35 kg of fuel exposed to 25,000 Mwd/ton and decayed for 90 days.[4]

Another major facility for the development of the thorium-uranium fuel cycle is the planned Babcock & Wilcox Nuclear Development Center to be completed in Lynchburg, Va., by 1965. The facility has been designed primarily to develop recycled fuels and will have the capability of testing fuels in an operating-reactor environment. In addition to manufacturing full-size thorium oxide elements, the facility will be expected to investigate other fuels, including plutonium.[5]

Foreign Plans

France has announced the start of construction of a processing facility, capable of handling

several hundred pounds of unirradiated uranium scrap per year.[6] The facility, which is being built at the Cadarache Research Center for operation by early 1964, will contain three recovery installations. In addition to the recovery facilities, the Cadarache installation will have processing facilities to convert uranium hexafluoride to metal and to ammonium diuranate. Two of the recovery installations will use conventional aqueous processing methods. Of these, one for uranium enrichments up to 3% will have a capacity of 30 kg/day; the other for high enrichments will have a capacity of 5 kg/day. The third recovery installation, which will be comparatively small (capacity 50 to 100 kg/year), will use a new dry process developed jointly by the French Commissariat à l'Énergie Atomique (CEA) and the French Chemical Company Kuhlmann. In this process alloying metals such as zirconium and aluminum are separated from the uranium by treatment with gaseous hydrogen chloride; then the uranium is treated with gaseous fluoride to obtain uranium hexafluoride. This process is similar to one under development at Argonne National Laboratory (ANL) for application to irradiated, spent fuels (see Sec. III of this issue).

In Italy, site preparation has started for the thorium-fuel-processing facility that Allis-Chalmers has designed for the Comitato Nazionale per l'Energia Nucleare (CNEN), Italy's AEC.[7] It will be built at Policoro on the instep of the Italian boot. Plant design is nearly completed, equipment procurement is under way, and startup is scheduled for July 1964. The plant will have a capacity of 15 to 30 kg/day and will be built and operated jointly by Allis-Chalmers and CNEN to process and refabricate Elk River (Minnesota) reactor fuel and possibly fuel from the SENN (Società Elettronucleare Nazionale) reactor near Punta Fiume, Italy. AEC has concluded an agreement with CNEN, whereby the Italians will process and refabricate the Elk River reactor's first core and provide AEC with technical information on thorium fuel technology.[2]

Construction was scheduled to start on Italy's EUREX chemical processing plant in January 1963. This facility, which will be capable of processing highly enriched uranium fuel elements from research and test reactors, will be located at Saluggia near the SORIN Nuclear Research Center. The plant has been designed by Vitro Corporation in cooperation with CNEN's fuel-element processing laboratory.[7]

Construction of the Eurochemic processing plant at Mol, Belgium, has made considerable progress according to a paper by R. O. R. Brooks, Technical Secretary of the Eurochemic Company.[8] In this paper Brooks reviews the progress of the development work on problems related to processing and gives a short account of the status of construction at the Eurochemic site. A number of buildings in the complex have been completed or nearly completed. Construction of the main process building and other technical buildings has commenced.

The Japan Atomic Fuel Corporation is planning construction of a major fuel-processing plant, reportedly to have a capacity in the range of 0.7 to 1.0 ton of uranium per day.[9] Seven chemical plant designers—four of them U. S. firms, two British, and one French—are said to be competing for a contract to design the plant, which would process both natural-uranium fuel to be used for Japan's Calder Hall type nuclear plant and enriched fuel (up to 5% U^{235}) clad in stainless steel or zirconium. Early in 1962 a special advisory committee to the Japanese AEC recommended that a processing plant be ready to begin operations in 1968.

Fuel-Cycle Economics

Plutonium-Uranium Fuel Cycle

Zebroski and coworkers at the General Electric Company have recently presented a preliminary process design and economic evaluation of the fuel cycle for a fast reactor using mixed PuO_2-UO_2 ceramic fuel.[10] The study is based on a reactor design that uses an average fuel exposure of 100,000 Mwd/ton, an average specific power of 1 Mw/kg, and a breeding ratio of 1.2. A design for a fast ceramic reactor of this type had been reported previously by Horst et al. of General Electric.[11] Capsule irradiations to 100,000 Mwd/ton on mixed PuO_2-UO_2 fuels have been done at operating temperatures for preliminary confirmation of the fuel concept.

The current paper includes an analysis of fuel refabrication processes and chemical separation processes. For processing of spent fuel, both solvent-extraction processes and anion-exchange processes were evaluated for installed

nuclear capacities ranging from 500 to 3000 Mw(e). If 1000 days of fuel irradiation and 90 days of cooling are assumed, decontamination factors between 3×10^7 and 3×10^8 are required. Solvent-extraction processes require preliminary decontamination steps to limit the radiation decomposition of the solvent. Cost data for solvent-extraction processes were not reported. A reference-design process flow sheet based on the anion-exchange process was derived for a 150 kg/day plant throughput. Capital and operating costs were estimated for three rates of throughput. The resulting chemical processing costs ranged from 0.27 mill/kw-hr for 500 Mw(e) of reactor capacity to 0.10 mill/kw-hr for 3000 Mw(e) of capacity.

For the fuel-element refabrication portion of the fuel cycle, analyses indicated that conventional glove-box handling procedures for plutonium fabrication could be adapted to accommodate the added radiations from recycled plutonium fuel. Four fabrication processes were evaluated, but none showed marked economic superiority over the others. A process based on pressing and sintering of fuel pellets was chosen as a reference.

For a production rate corresponding to 3000 Mw(e) of generating capacity, the estimated fuel-fabrication cost is 0.29 mill/kw-hr, or $211 per kilogram of uranium and plutonium in the core region (excluding axial and radial blankets), or $1.06 per gram of plutonium content. Radial blanket fabrication cost was estimated at $49 per kilogram of uranium.

The fuel-cycle cost for a 500-Mw(e) reactor, using the processes described and July 1962 economic conditions, is as follows:

	Mills/kw-hr
Fuel fabrication	0.46
Processing and shipping	0.27
Plutonium inventory charge	0.18
First-core capitalization	0.18
Plutonium credit	(–0.08)
Total fuel-cycle and first-core capitalization	1.01

For processing rates corresponding to a capacity of 3000 Mw(e), the total fuel-cycle cost becomes 0.74 mill/kw-hr.

Thorium-Uranium Fuel Cycle

In a recent paper Edlund of the Babcock & Wilcox Co. has discussed the economic aspects of the thorium fuel cycle.[5] Included in the paper is an analysis of fabrication and processing costs for a Spectral Shift Control Reactor (SSCR) using thorium oxide fuel mixed with highly enriched uranium. The uranium is a mixture of the isotopes U^{233}, which is bred in the reactor, and U^{235}, which is added to make up for the net loss of fissionable material.

The spent cores from the reactor would be chemically processed to separate the uranium as uranyl nitrate from the thorium and fission products. Edlund proposes to recycle only the uranium and to store the thorium for a period of approximately 12 years so as to permit the Th^{228} to decay. If the thorium is assumed to have zero value when it is sent to storage, the economic penalty is estimated to be only 0.06 mill/kw-hr. The separated uranyl nitrate would be sent to a fuel-fabrication plant where thoria-urania powder would be produced by the sol-gel process and loaded into tubes by vibratory compaction.

One of the problems associated with the thorium fuel cycle is the production of U^{232} which decays to daughter products that emit intense gamma radiation. Edlund proposes that the uranyl nitrate be processed in a small ion-exchange unit to strip the daughter products that have built up in the uranium during the time interval between processing of the spent cores and receipt of the material at the fuel-fabrication plant. Cleanup and maintenance of the fabrication equipment would be scheduled weekly to permit direct maintenance and repair. Assembly of the fuel elements would require some shielding, which might be provided by mechanical assembly under 2 ft of water.

Edlund estimates that by 1968 a recycle fabrication plant serving three large reactors could fabricate oxide fuel elements at a cost of $80 per kilogram of contained thorium. The processing, transportation, and insurance charges are expected to add another $40 per kilogram to the cost. A recycle plant in operation by 1968 would be expected to serve six large reactors by 1972 with further savings in costs. The resulting fuel-cycle costs for an average fuel exposure of 25,000 Mwd/ton are estimated as follows:

	Mills/kw-hr
Fuel fabrication	0.45
Processing	0.16
Transportation and insurance	0.07
Inventory charge, 7% (80% load factor)	0.53
Fissionable material makeup	0.16
Total	1.37

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Few new developments have been described recently in methods for placing reactor fuels in aqueous solutions suitable for solvent extraction. The applications of solvent extraction are broadening, especially with respect to the variety and effectiveness of reagents capable of forming stable metal-ion complexes.

Preparation for Fuel Processing

The means for preparing reactor fuels for recovery include mechanical or chemical removal of cladding or structural materials, acid dissolution of cores or entire elements, and leaching of desired materials from fuel units.

Chemical Removal of Cladding Materials

Dilute (4*M* to 6*M*) sulfuric acid has been used to dissolve cermet fuel elements with a stainless-steel matrix and cladding[1] and has been investigated extensively for removal of cladding from uranium dioxide pellet fuel elements that are clad with stainless steel.[2] A problem in this process is the occasional passivation of the stainless steel by low concentrations of nitric acid in the dissolving reagent. Katz[3] has taken advantage of this difficulty in devising a novel method for carrying out such decladding operations in a stainless-steel vessel. A low concentration of nitric acid (0.04*M* to 0.08*M*) is maintained in the boiling dissolving reagent (6*M* to 7*M* sulfuric acid) to inhibit attack of the latter on the stainless-steel vessel. The fuel to be declad is contained in a Nionel basket, which is kept from making contact with the stainless-steel vessel. Passivity of the fuel-element cladding surface is overcome by maintaining some or all of the fuel units in contact with a less noble metal such as mild steel or Nicrobraz 10, a brazing alloy used in element fabrication. Since hydrogen is evolved in dissolution, an adequate nitrate concentration is maintained in the dissolvent by use of a downdraft condenser for vapors evolved. About 15% oxygen must be maintained in the gas phase in the condenser to ensure conversion of nitric oxide and its subsequent absorption in the condensate. The process has been studied principally on a laboratory scale, and the necessity for close control of concentrations has been indicated, but more than 100 lb of stainless steel has been dissolved on a pilot-plant scale without serious vessel corrosion. Since nitrate-bearing sulfuric acid attacks uranium dioxide, sulfamic acid must be added to the dissolvent to reduce uranium loss from the core material.

Dissolution of Fuel Cores

An important step in the shear-leach process for stainless-steel-clad uranium dioxide pellet fuel, which is being developed at Oak Ridge National Laboratory (ORNL), is the dissolution of the sheared pellet fuel in nitric acid. This is done in a multistage countercurrent dissolver. Johnson[4] has recently completed a theoretical treatment of the countercurrent leaching process, assuming a zero-order reaction, and has calculated rate coefficients with 5.5*M* to 8.0*M* nitric acid. A computer calculation for the system agreed well with data from eight batch countercurrent runs made in the laboratory. An analog computer representation of the process was also developed and tested against the laboratory results.

Dissolution of Ceramic Fuels

In other work at Oak Ridge, studies are being made of the dissolution of ceramic fuels composed of uranium and plutonium dioxides in

nitric acid with various added reagents. In dissolving uranium dioxide the addition of moderate to high concentrations of sodium or lithium nitrates yielded corresponding dissolution rates for equivalent nitrate concentrations.[5] Dissolution of plutonium dioxide pellets in 7*M* and 14*M* nitric acid was quite slow but was somewhat accelerated by addition of 0.005*M* to 0.1*M* hydrofluoric acid with 0.015*M* to 0.3*M* aluminum nitrate.[6] Dissolution was further accelerated in the absence of aluminum ion. Pellets composed of 20% plutonium dioxide–80% uranium dioxide dissolved rapidly and uniformly in 10*M* nitric acid containing 0.5*M* hydrofluoric acid.[7]

Total Dissolution of Metallic Fuels

With an increasing use of Zircaloy-clad zirconium-uranium alloy fuels in naval propulsion reactors, a need has developed for an economic and more broadly applicable process facility of greater capacity for such fuels than that of the small-scale plant currently in existence at the Idaho Chemical Processing Plant (ICPP).[8] Rohde[9] reports on the basis of laboratory studies that the existing hydrofluoric acid process can be modified for this purpose to permit continuous dissolution with the use of a dilute process. At a fluoride-to-zirconium mole ratio of 5 and a total fluoride concentration of 5.3*M*, Zircaloy is attacked at a rate of 12 mg/(cm^2)(min), which is satisfactory for continuous equipment. Studies of the solubility of uranium tetrafluoride in the dissolver product solution indicate that the uranium from fuels containing up to about 2% uranium could be retained in solution without the use of an oxidant, thereby minimizing corrosion problems. The dilute process does not result in larger extraction-process volumes or waste volumes than those obtained with the earlier process, since the dissolver product must be made up to an adjusted feed whose composition is dictated by stability toward precipitation. Boric acid, which might be used for criticality control in a continuous process, does not significantly affect the rate of dissolution; boric acid concentrations up to 2 g of boron per liter were tested.

In the course of this work, it was also noted that a solution containing hydrofluoric acid, nitric acid, and aluminum nitrate in proportions corresponding to the fluoride and nitrate content of adjusted feed also dissolved zirconium at a reasonable rate.[10] Since such compositions containing dissolved zirconium are relatively noncorrosive to stainless steels, the process might be a useful alternative to dissolution in hydrofluoric acid.

Electrolytic Dissolution of Stainless-Steel and Cermet Fuel

Studies have previously been described on the electrolytic dissolution of stainless-steel–uranium dioxide cermet fuels in nitric acid.[11] Logsdail of the United Kingdom Atomic Energy Research Establishment (AERE) has reported similar work.[12] Both stainless-steel and cermet pellets were electrolytically dissolved from a tantalum anode basket into an electrolyte of 0.5*M* to 6.0*M* nitric acid containing 20 g of stainless steel per liter. Above 2*M* nitric acid the dissolution rate was proportional to the current density, and the cell drop was about 0.12 volt/amp. With 6*M* nitric acid, current utilization was 100%. Provision for vibration during dissolution appeared to be desirable, and some black sludge (containing significant amounts of iron, chromium, nickel, and silicon) was observed, especially at low acidity. The uranium dioxide dissolved from the cermet at approximately the same rate as the stainless steel.

Dissolution of Silicon-Containing Fuel

Fuel for the General Electric Test Reactor (GETR) is an aluminum-clad aluminum-uranium alloy plate wherein about 2% silicon is contained to improve the metallurgical properties of the alloy. In addition to the surface-active properties of silica produced upon dissolution in nitric acid, which may provide an operational problem, preliminary data from General Electric indicated that uranium in the fuel might form an insoluble compound with the silicon or that soluble uranium might be irreversibly absorbed on silica after dissolution. Bower[13] reports from the ICPP that laboratory tests showed that such phenomena did not occur and that uranium occluded on siliceous residues could be recovered in the normal extraction process without unusual loss. Increased amounts of interfacial emulsion were observed with freshly prepared silica-bearing feeds, as compared with aqueous feeds containing no silica.

Treatment of Graphite and Carbide Fuels

The British have recently released a report that describes processing studies on carbide-

graphite fuels such as might be used in a high-temperature gas-cooled reactor.[14] The fuels consisted of uranium and thorium (presumably as carbides) and graphite and were prepared either by compaction and firing of the mixed powders at 1400°C or by impregnating a previously baked mixture of thoria, coke, and pitch with uranyl nitrate and graphitizing the mass. The recovery methods that were investigated included oxidation and ash dissolution, acid leaching, anodic disintegration, and treatment with bromine or bromine trifluoride.

Laboratory tests indicated that oxidation at 700°C, followed by dissolution of the ash in nitric-hydrofluoric acid, was feasible and that uranium and thorium recovery was quantitative. Small amounts of insoluble residues remained which contained no uranium and thorium. It was noted that large volumes of off-gas would be generated and that scrubbing of the gases would probably be required. This problem was not studied, however.

Uranium was almost quantitatively recovered from the crushed, compacted fuel by leaching several hours with 4*N* nitric acid, but some of the thorium remained undissolved unless a low concentration of hydrofluoric acid was added. Recovery was less quantitative from the impregnated and graphitized samples. Anodic disintegration instead of mechanical fracturing could be used to make the uranium and thorium more accessible but did not of itself ensure quantitative recovery. In leaching irradiated fuel samples, the uranium was recovered quantitatively with 2*N* nitric acid; but thorium, protactinium, and most fission products were incompletely removed.

Treatment with halogen reagents was only briefly studied. Bromine trifluoride reacted vigorously or inflamed, and the uranium was volatilized as the trifluoride. Treatment with bromine vapor did not increase surface area or improve recovery upon nitric acid leaching.

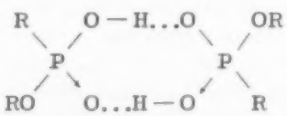
Other workers are showing considerable interest in the treatment of carbide fuels. Baudin[15] notes that the neutral or acid hydrolysis of uranium carbide leads to a complex mixture of saturated hydrocarbons and ethylene and that an oxidant increases the concentration of unsaturated hydrocarbons. At Oak Ridge, work has continued on studies of carbide hydrolysis.[7] Treatment of a uranium dicarbide (composition corresponding to $UC_{1.91}$) with water yielded a gas consisting of about one-half hydrogen and accounting for one-third of the carbon. Another third was present in a waxy material. Temperatures in the range 25 to 99°C had no effect on the products of the reaction. Sasaki[16] treated thorium dicarbide with hydrochloric, sulfuric, and nitric acids at room temperature and at 80°C. Complete dissolution in 0.5*N* to 12*N* hydrochloric acid was obtained in 24 hr at room temperature. In dilute sulfuric acid, thorium carbide dissolved completely but was only partially dissolved at room temperature as the acid concentration was raised, presumably due to a limiting solubility of thorium sulfate. With nitric acid at room temperature, the solubility of the dicarbide also decreased as the acid concentration was increased from 1*N* to 6*N* but increased again as the acid concentration was further raised. Kibbey and Ferris,[17] in reporting work at ORNL, note that electrolytic disintegration is ineffective in recovering uranium from particles of uranium carbide coated with 55- to 60-μ layers of pyrolytic carbon.

Separations Processes

Solvent-Extraction Processes

Significant recent developments in the science and application of solvent-extraction techniques in nuclear fuel processing, both in this country and abroad, were discussed in a recent meeting at Gatlinburg, Tenn. (Solvent Extraction Chemistry Symposium, October 23–26, 1962, sponsored by ORNL). It is planned to publish many of the papers in *Nuclear Science and Engineering*. Some pertinent information from the discussions, together with other reports of advances in this area of technology, is given in the following subsections.

Basic Studies. Peppard[18a] discussed the nature of the extractable complexes formed between polyvalent metals and acidic phosphate and phosphonate esters. For example, monoacidic phosphates and related compounds appear to dimerize as follows in a diluent system:



The number of such dimers associated with the metal complex with tracer-level actinides and

lanthanides is equal to the valence of the metal ion. In the case of divalent metals such as calcium, the extractant dependency, and presumably the number of dimer molecules bound in the complex, varies from 2.5 to 3, depending on the nature of the organic radical. Similarly, monoacidic phosphorus compounds are more highly polymerized and behave as liquid ion-exchange materials. The state of aggregation varies with the nature of the solvent and of the organic radicals. Further information on the nature of the complexes formed in such systems, as deduced from spectroscopic studies, was presented by Ferraro.[18b]

In continuing this subject, Hardy[18c] reported work from Harwell on alkyl phosphoric acid complexes. His studies led to an explanation of the formation of solids under acid conditions in degraded TBP-diluent systems in the presence of significant concentrations of zirconium as a result of the formation of polymeric complexes. At low acidity Hardy felt that the complex formed between the first degradation product of tributyl phosphate (TBP), dibutyl phosphoric acid (HDBP), and zirconium was a simple association of two HDBP dimers with a nitratozirconyl ion. Higher acidity is presumed to favor the forming of monomeric dibutyl phosphate units with zirconium and the linking of the zirconium atoms alternately with phosphate residues into long chains. The latter complex is presumed to be a highly insoluble material.

Davis has recently reported extensive physical and thermodynamic data applying to the extraction of nitric acid by TBP in a hydrocarbon diluent.[19–21] An equation was developed to correlate equilibrium data, and molal volumes and activity coefficients were determined. The transfer of water into a solution of TBP in hexane was studied by Olander and Benedict,[22] who noted that the process appears to be simply one of mass transfer.

Baes[18d] discussed the phenomena of synergism in organophosphate extraction, in which extraction coefficients for metal ions (MO_2^{2+}, for example) with a solvent containing a dialkyl phosphoric acid (HA) and a neutral organophosphate (B) are considerably greater than the sum of the extraction coefficients for the separate reagents. Such synergism is attributed to the formation of a mixed extraction complex containing both HA and B. It is not yet possible to determine if the mixed complex is an addition product such as $MO_2(A_2H)_2B$ or a substitution product such as MO_2A_3HB. Some observations are consistent with the formation of an addition product. A paper by Healy[18e] was devoted to synergism involving thenoyl trifluoroacetone (TTA) and neutral phosphates. Extremely large effects of enhanced extraction, by factors of up to 10^8, have been observed. Systems studied have included uranyl, plutonyl, and higher transuranic species, with TBP, trioctyl phosphine oxide, and other reagents.

Irving and Edgington have reported extensive studies on synergistic effects among the actinides in valence states varying from 3 to 6, either tributyl phosphate or tributyl phosphine oxide, and TTA.[23–25] Enhanced extraction appears to depend on the ability of the actinides to achieve a coordination number of eight. According to their behavior, the formulas of some typical mixed complexes were as follows:

PuO_2, 2TTA, TBP
$HNpO_2$, 2TTA, TBP
$Th(TTA)_3NO_3$, TBP or TBPO
$Am(TTA)_3$, 2TBP
$Am(TTA)_2NO_3$, 2TBPO

Taube has also reported work on the phenomenon of synergism in plutonium extraction.[26] A variety of other combinations of synergists and complexing reagent was investigated, and the effect of nature of the diluent was examined.

Degradation and Treatment of TBP Process Solvent. Lane reported Harwell studies on the degradation of the hydrocarbon diluent used with TBP in extraction processes.[18f] The performance of diluents has been rationalized on the basis of their composition, their reaction with nitrous acid, and the subsequent reaction of nitroparaffins with acids and alkalies. It is believed that nitrous acid is the material primarily responsible for diluent degradation. There is evidence that the species responsible for the retention of zirconium in degraded solvents are hydroxamic acids; these can be formed from nitroparaffins under process conditions. Removal or destruction of the primary nitroparaffins is essential in any effective solvent treatment process.

Blake discussed Oak Ridge work that confirmed the major role of nitroparaffins as the principal significant diluent degradation product and noted that the extraction behavior of degraded solvents is consistent with their known

chemistry.[18g] He also stated that acid treatment and irradiation exposure in a two-phase system produced the same type of solvent deterioration; under the conditions of degradation, 100 watt-hr/liter was essentially equivalent to 11 hr of boiling with 2*M* nitric acid, as shown by zirconium-niobium extraction, total organic nitrogen content, and spectral absorption characteristics.

Retention of uranium and plutonium by degraded solvents is largely attributed to the presence of monobutyl and dibutyl phosphoric acids. Kennedy[27] notes that ready and complete removal of uranium from badly degraded solvents can be accomplished by adding peroxide to caustic or sodium carbonate wash solutions, whereas plutonium removal is best effected by adding a low concentration (perhaps 0.01*M*) of a tetravalent uranium solution to a dilute nitric acid washing reagent.

Workers in Japan have also considered the effect of irradiation in damaging solvent-diluent systems. Ishihara and others[28] confirm the results of others in reporting that increased irradiation, up to the order of 100 watt-hr/liter, principally produces marked changes in the distribution coefficient for zirconium and niobium in a system consisting of an aqueous phase in contact with TBP-kerosene solvent. Increased times for phase separation were also noted. Related work by some of the same authors upon alkyl amine solvent systems indicated that the amine solvents were little affected by irradiation[29] up to 10^8 r.

Alternate Solvent Systems. A number of types of organic compounds, other than the well-known hexone and TBP, show considerable promise for practical extraction processes for either heavy metals or fission products. Many of these were discussed at the Gatlinburg meeting.

Siddall of Savannah River described a novel class of organophosphorus compounds — bidentate compounds — now being investigated as extractants.[18h] These materials form very stable complexes, presumably as a result of their chelating nature, which is apparent in the following example that shows methylene diphosphonate:

$$(RO)_2\,P(=O)-CH_2-P(=O)\,(RO)_2$$

In equilibrium with nitric acid solution, these compounds may show high distribution coefficients for trivalent actinides and lanthanides at high acidity. For example, with a solvent containing tetrabutyl methylene diphosphonate, a distribution coefficient of about 100 was observed for cerium. Because of solubility problems, tetraamyl methylene diphosphonate may be a better extractant for removing small residues of trivalent actinides and lanthanides from waste concentrates.

Other phosphorus compounds continue to be of interest. Manning[30] reports distribution data for thorium and a series of lanthanides into a 58 vol.% solution of dibutylbutyl phosphonate (DBBP) in kerosene and suggests that the latter might find ready application in the separation of thorium from rare earths on an industrial scale. Handley at the Gatlinburg meeting[18i] noted that the dialkyl phosphothioic and -dithioic acids, which are related to, for example, dibutyl phosphoric acid, provide distribution coefficients that are an order of magnitude higher than the latter. Their use, however, is limited by a lower degree of stability and by the fact that they are fairly strong reducing agents.

Simple oxygenated compounds are much less powerful extractants but may nevertheless possess definite areas of utility. The diethers, which are relatively resistant to nitric acid, have been investigated at Oak Ridge by Googin and others.[18j] Diethoxypentane was recommended as a potentially useful compound with low solubility in water. A Czechoslovakian worker, Starý, has noted that certain alpha hydroxy acids — glycolic, lactic, and hydroxyl butyric — form stable complexes with the uranyl ion, containing one, two, or three molecules of acid per uranyl group.[31]

Several papers at the Gatlinburg meeting were devoted to studies and applications of alkylamines as extractants, including the presentation of two detailed process flow sheets. Coleman[18k] noted that the high-molecular-weight amines and quaternary ammonium compounds appear to form adducts with metal ions, similar in character to the binding effected by ion-exchange resins. Acids, however, are extracted by simple salt formation. In the case of uranium extraction, there appear to be four to six amine molecules in a complex containing one atom of uranium. At low loadings a micelle may be formed which contains the salt sur-

rounded by amine molecules. Keder[18l] described studies which indicate that trioctylamine extracts trinitrato and hexanitrato species of the tetravalent actinides, and a tetrachloro species.

The first amine process flow sheet was described by Chesne of the French Atomic Energy Authority.[18m] This process uses trilaurylamine (TLA) (0.15*M* in dodecane) to concentrate and complete decontamination of plutonium recovered from irradiated fuel and separated from uranium in one or two Purex (TBP extraction) cycles. The 2.0*M* nitric acid feed solution is a product of the Marcoule plant obtained after precipitation of plutonium as the hydroxide and contains perhaps half as much uranium as plutonium (about 1.4 g of plutonium per liter). Extraction is carried out in mixer-settlers using only one-tenth volume of solvent per volume of feed. The loaded solvent may be washed with dilute nitric acid before stripping with one-tenth its volume of a dilute mixture of sulfuric and nitric acids. The product concentration may reach 20 g of plutonium per liter.

Tetravalent plutonium is quantitatively extracted by this process, and decontamination from zirconium by a factor of greater than 10^4 is effected. The plutonium stream is concentrated about 100-fold and separated from uranium by a factor of 600.

In extraction with the simple amine-diluent mixture, saturation of the solvent with plutonium may easily be exceeded, and a third liquid phase may separate. The tendency for this to occur may be reduced markedly by adding 5% of octanol-2 to the solvent, which increases the permissible plutonium loading from 2 to 9 g/liter.

In comparative studies of the stability of the amine solvent toward irradiation (50 watt-hr/liter level) relative to that of a TBP-diluent mixture, no effect on the extractability of tetravalent plutonium was noted for TLA, whereas the TBP solvent was markedly affected.

The other process flow sheet was that of the EUREX process that was described by Calleri as applicable to aluminum-clad uranium-aluminum alloy dissolved in nitric acid.[18n] The solvent is composed of 4% of the tertiary amine Alamine 336 dissolved in a commercial mixture of trimethyl benzenes. The feed is composed of 1.7*M* aluminum nitrate containing 1.3*M* nitric acid; such a concentration of aluminum nitrate is required as a salting agent to achieve adequate uranium recovery. In laboratory studies of a two-cycle process, overall log beta and gamma decontamination factors of 6.9 and 6.6 have been achieved.

Solvent degradation in this system results in the production of secondary amine and in sharply decreased zirconium decontamination. The amount of deterioration is decreased in the presence of aqueous feed, and the adverse effects are readily removed by a caustic wash.

The expected advantages of this new flow sheet are connected with solvent stability to irradiation and the high selectivity of the amine solvent which permits a high decontamination factor and therefore a reduction in the number of extraction cycles as compared with TBP processes.

Higher alkylamines are also being considered as solvents. Calleri and others, in recently released Eurochemic reports,[32,33] gave data on the distribution of uranyl nitrate between 0.1*M* and 4*M* nitric acid and a 10% solution of trilaurylamine in a paraffinic hydrocarbon solvent containing some octanol. It appeared that the extracted species was a tetranitratouranyl ion above 2*N* nitric acid and that two amine molecules were associated with one uranyl group.

Plant and Equipment Design and Operation

For use in dilute Purex-process flow-sheet studies, Ryon reports on the performance of nozzle-plate pulse columns.[34] Compositions of the test solutions are shown in Table II-1.

Two 24-ft test columns, one equipped with nozzle plates having 0.125-in.-diameter nozzles and 10% free area and the other equipped with nozzle plates having the same size nozzles but 23% free area, were used either as compound extraction-scrub columns or as simple extraction columns in the flooding tests. The nozzles were oriented down for solvent-continuous operation (bottom interface). Flooding always occurred at the feed point, and the flow capacity reported is the total flow in the extraction section. The nozzle plates (0.125-in.-diameter nozzles, 10% free area) in the 12-ft stripping column were oriented upward for aqueous-continuous operation (top inter-

Table II-1 PHYSICAL PROPERTIES OF TEST SOLUTIONS

Test solution	Uranium concentration, g/liter	Acidity, M H^+	Density, g/cm^3	Viscosity, centipoises
Feed (AF)	65	2.0	1.16	1.12
Scrub (AS)	0	3.0	1.09	0.97
Solvent (AX)			0.814	1.63
Raffinate (AW)	0.006	1.9	1.06	1.12
Loaded solvent (AP)	75.6	0.20	0.934	2.67
Strip reagent (CX)		0.01		
Stripped solvent (CW)	0.0002	0.02	0.814	1.63
Uranium product (CP)	38.9	0.112	1.05	0.94

face). Flooding occurred at the bottom of the column.

It was reported that flow capacity for a 23% free-area nozzle plate increased as the pulse frequency dropped. The flow capacity of the compound extraction-scrub column at 35 cycles/min for the dilute Purex-process flow sheet was less than half the capacity under standard flow-sheet conditions. These data are presented in Table II-2.

In-Line Conductance Analyzer

Hahn[13,35] reports on an in-line product analyzer development for possible use with electrolytic dissolvers. The principle of operation involves the simultaneous determination of the conductance of two samples of process solution, one at full concentration and one diluted one-to-one with water.

A schematic drawing of the instrument is shown in Fig. II-1. The flow rates of the solution (A) and water (B) streams are governed by the streams' passages through capillary tubes (C) under a fixed hydrostatic head (D).

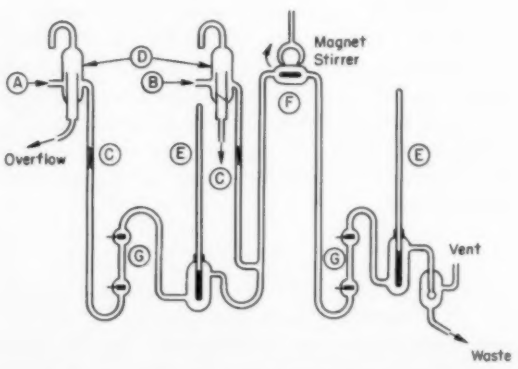


Fig. II-1 In-line conductance analyzer.[13]

Thus the volume ratio of the two streams will depend on their densities and viscosities, which in turn depend on temperature and solution composition. If the temperatures (E) of the streams are controlled, the composition of the mixed solution will be reproducible. The mixing chamber is shown at (F), and the conductance cells are shown at (G).

The instrument was calibrated using appropriate solutions, and Fig. II-2 shows a plot of specific conductances vs. specific gravity for the calibrating work.

When the instrument was used for several weeks with a bench-scale electrolytic dissolver, operations were satisfactory except for minor trouble with particles clogging the capillary.

It appears that the simultaneous measurement of these solution properties would also provide estimates of metal and nitric acid content over most of the composition range.

Countercurrent Liquid-Liquid Extractions in Annulus Columns with Shearing Motion

Spence and Streeton of AERE[36] have done some very extensive work on a laboratory-size liquid-liquid extraction column of annular cross section with a shearing motion.

They point out that, if the annulus is formed by two cylinders and the inner one rotates (see Fig. II-3), then a series of pairs of oppositely rotating vortices are set up if the speed exceeds a certain value. These vortices were made visible by injecting dye. With a two-phase flow, these become clearly visible without dye.

The first experiments were made with smooth cylinders, but it was later found that fins which combined pairs of vortices improved the performance. Although this work only covered small-diameter apparatus (up to 5-in.-diameter inner cylinder), calculations were made to show

Table II-2 FLOODING RATES FOR NOZZLE-PLATE COLUMNS

(Pulse Amplitude: 1 in.)

Pulse frequency, cycles/min	Nozzle-plate free area,* %	Column operation	Continuous phase	Flooding rate, gal/(sq ft)(hr) Dilute Purex	Flooding rate, gal/(sq ft)(hr) Standard Purex
		Extraction Columns			
35	23	Compound	Solvent	875	
50	23	Compound	Solvent	535	
70	23	Compound	Solvent	<420	
35	23	Simple	Solvent	875	1530
50	23	Simple	Solvent	680	880
35	10	Compound	Solvent	<500	1160
50	10	Compound	Solvent	<420	790
35	10	Simple	Solvent	560	
50	10	Simple	Solvent	350	
		Stripping Column			
25	10	Simple	Aqueous	1170*	1370
35	10	Simple	Aqueous	840*	1120
50	10	Simple	Aqueous	600*	550

*Nozzles oriented down except in dilute Purex stripping-column tests.

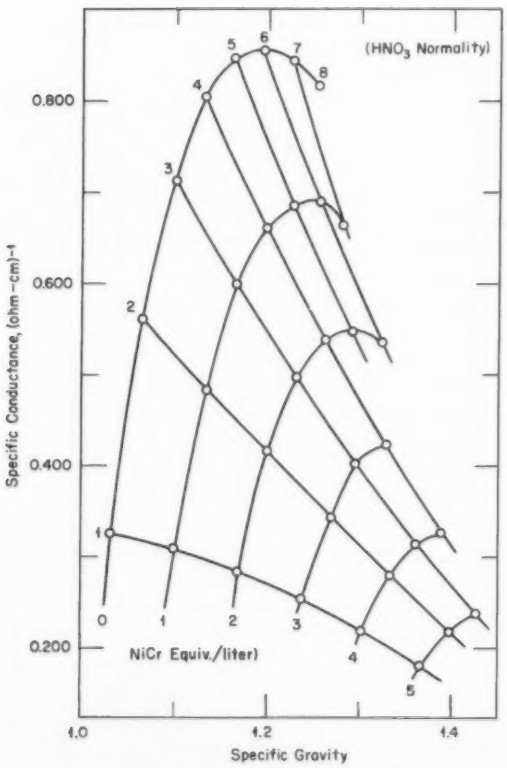


Fig. II-2 Specific conductances of nitric acid–Nichrome nitrate mixtures[35] at 25°C.

that a 21-in.-ID outer cylinder with an 18-in. rotor could handle 120 lb/hr. The speed required was estimated at 33 rpm.

The report presents fairly detailed data on laboratory-size columns, both smooth and finned, for a butex-nitric acid system. An expression is derived for the height equivalent of a theoretical stage (HETS) as follows:

$$H = \text{constant}\left(d^4 + \frac{R_1^2 d^2}{3}\right)^{1/6}$$

where R_1 is the radius of the rotor and d is the width of the annulus. It was shown that the expression holds over the range studied: R = 0.075 to 6.66 cm, d = 0.05 to 1.6 cm.

In general, a rotor speed to produce a peripheral velocity of 75 to 85 cm/sec was required to produce the vortices and efficient operation. Any increase in speed beyond this only increased holdup. Figure II-4 shows this dependence on rotor speed. Figures II-5 and II-6 show some of the data on the variance of stage height.

Hydroclone Extraction

An interesting variation of hydroclone extraction is presented in a British patent.[37] The basic unit consists of two hydroclones. The two immiscible liquids are fed to the inlet of the first hydroclone, which has overflow and underflow

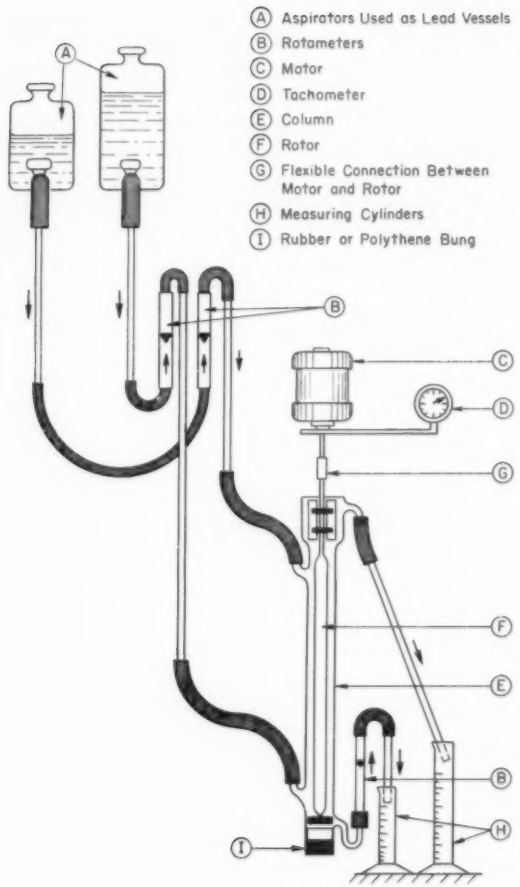


Fig. II-3 Apparatus for liquid-liquid extraction studies in annulus columns with shearing motion.[36]

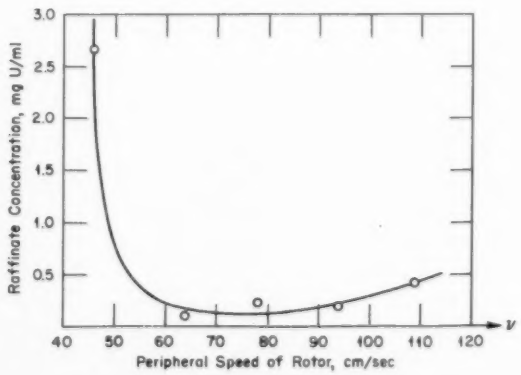


Fig. II-4 Dependence of extraction efficiency on rotor speed.[36]

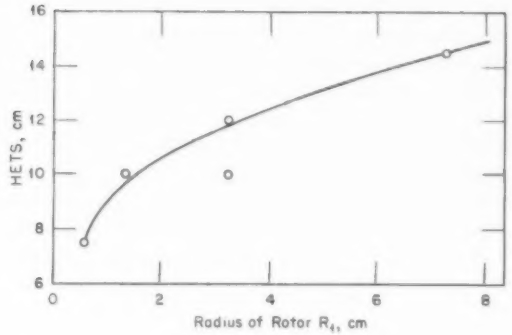


Fig. II-5 Effect of increase of rotor diameter for constant annulus (d ~ 0.5 cm).[36]

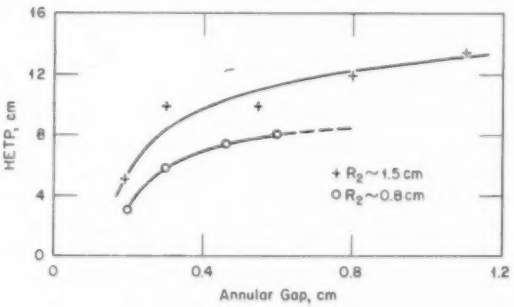


Fig. II-6 Effect of increase of annulus for constant stator diameter.[36]

outlets. One of these is relatively large compared with the other. One of the liquids is then withdrawn substantially free from the other at the small outlet. A mixture of the liquids is withdrawn from the large outlet and fed to the inlet of the second hydroclone, which has overflow and underflow outlets in inverse size relation; thus the other liquid can be withdrawn in a fairly pure state from the smaller outlet. A mixture will be withdrawn from the larger outlet of the second hydroclone and recirculated back to the inlet of the first. This then forms a single extraction unit and could be made multistage by addition of pairs of hydroclones.

Corrosion and Construction Materials

Some power-reactor fuels, either proposed or in use, have compositions markedly different

from those for which the AEC processing plants were designed. In order to handle these newer fuels in the existing plants, so-called head-end procedures have been developed by the various sites. These are capable of producing feed solutions that are compatible with the existing plants. Optimum construction materials for each of the head-end treatments have been determined in corrosion studies. Efforts at arriving at a compatible combination of processes and a common construction material are being made.

Corrosion of Stainless Steel in Nitrate Solutions

At Savannah River an electrolytic dissolution process for zirconium-clad, stainless-steel-clad, and stainless-steel matrix fuels is under development. Nitric acid is the proposed dissolution medium, and austenitic stainless steel is the proposed construction material. Nitric acid solutions containing electrolytically dissolved stainless steel are highly corrosive during evaporation at 100 to 120°C. At Savannah River hexavalent chromium has been identified as the ionic species responsible for the accelerating corrosion during evaporation.[38]

Recently two reducing agents, carbon and sulfur, have been found which inhibit the formation of hexavalent chromium and hence reduce the corrosion of austenitic stainless steels in boiling nitric acid.[39] When carbon or sulfur was added at a rate of 2 g/liter of boiling solution per day, corrosion by hexavalent chromium in 10*M* nitric acid decreased from 720 mils/year to less than 10 mils/year. These two materials have been found to be capable of reducing the hexavalent chromium content to below 0.001 g/liter (the lower limit of detection by the colorimetric analytical method used). Carbon appears to be compatible with the separations process; the oxidation products are gaseous, and the carbon has a half-life of about 10 hr in the boiling acid. The disadvantages associated with the use of sulfur as a reductant are that it floats on the surface of the solution, that it sublimes and subsequently condenses on the surfaces of the condensers, and that some of the oxidation products are sulfites which are potential solids. As a result, carbon was used as the reductant in most of the experiments.

Subsequent tests were made to determine the effect of carbon in acid containing dissolved stainless steel. It was found that, with carbon added as the reductant, the corrosion rate was higher in nitric acid containing dissolved stainless steel than it was in acid solutions containing only dissolved chromium. The mechanism of this attack is not known; however, some of the conditions affecting corrosion rate have been determined experimentally for types 304L and 309SCb stainless steels, as shown in Fig. II-7. When carbon is added, a high concentration

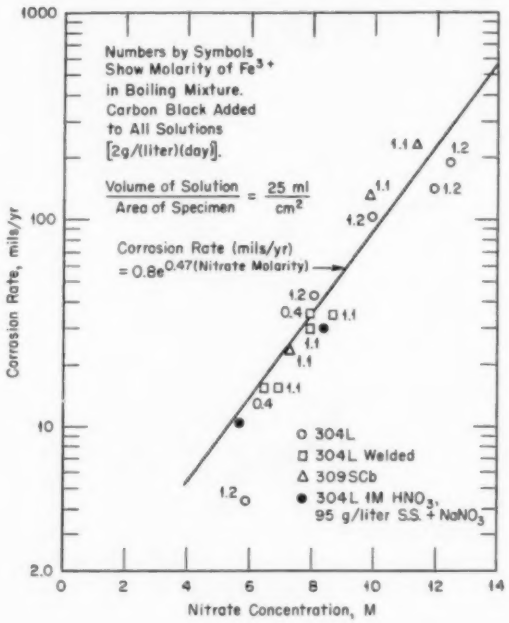


Fig. II-7 Corrosion of types 304L and 309SCb stainless steels in boiling solutions containing HNO_3 and dissolved stainless steel.[39]

(0.5*M*) of ferric ions and a total nitrate concentration in excess of 6*M* must be present before the corrosion rate exceeds 15 mils/year. It was found that total nitrate content rather than nitric acid concentration was important.

Additional tests were conducted in nitric acid solutions containing only dissolved iron (instead of dissolved stainless steel), and these results are shown graphically in Fig. II-8. The corrosion rates observed were nearly identical in the two systems. It was also found that, with only dissolved iron in the nitric acid, the corrosion rate was independent of whether carbon had or had not been added to the solution. The two conclusions from these series of tests were that (1) additions of carbon to chromium-

containing solutions eliminate the corrosion caused by hexavalent chromium and (2) the corrosion can be limited to 15 mils/year in iron-containing solutions (either with or without carbon additions) by keeping the total nitrate concentration below 6*M*.

An effort was made to apply these results on a larger scale in a stainless-steel pilot-

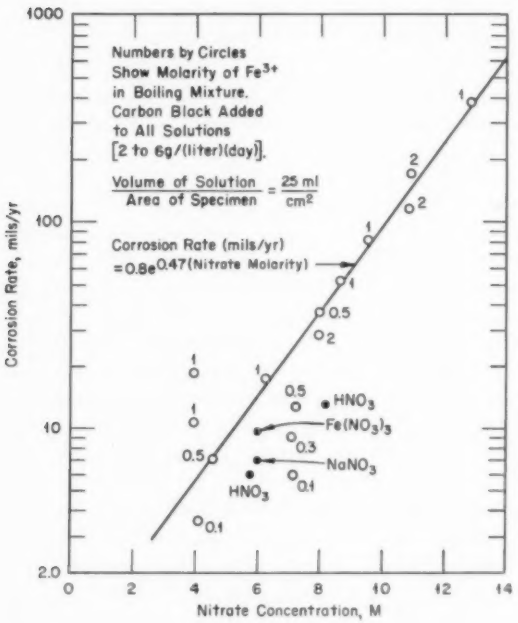

Numbers by Circles Show Molarity of Fe^{3+} in Boiling Mixture. Carbon Black Added to All Solutions [2 to 6g/(liter)(day)].
Volume of Solution / Area of Specimen = 25 ml / cm²
Corrosion Rate (mils/yr) = $0.8e^{0.47(\text{Nitrate Molarity})}$
Corrosion Rate, mils/yr
Nitrate Concentration, M
HNO_3
$Fe(NO_3)_3$
$NaNO_3$
HNO_3

Fig. II-8 Corrosion of type 304L stainless steel in boiling solutions[39] containing HNO_3 and Fe^{3+}.

plant evaporator used to process waste streams containing nitric acid, dissolved stainless steel, and other constituents.[39] Solutions of nitric acid containing various concentrations of dissolved stainless steel, with and without slurried graphite, were fed continuously to a 30-gal evaporator made of type 309SCb stainless steel and containing steam coils made of type 304 stainless steel. During these tests coupons of wrought and welded type 309SCb stainless steel were exposed in the liquid and vapor spaces. During the batch evaporation the total nitrate content varied from about 4*M* to 11*M*. Trivalent chromium concentration varied from 7 to 40 g/liter, and that of iron varied from 30 to 140 g/liter. In no single run was the hexavalent chromium concentration in excess of 0.005*M*; hence it appears that the presence or absence of graphite did not affect the results (later laboratory tests indicated that graphite is not so effective a reductant as carbon). To explain the absence of hexavalent chromium, the solutions were analyzed for reducing strength. It is postulated that the small quantities of nitrous acid found upon analysis were sufficient to retain all the chromium present in the trivalent state. The stainless-steel type 309SCb coupons (wrought) corroded at rates varying from 7 to 52 mils/year, whereas the stainless-steel type 304 steam coils corroded at rates of 100 to 250 mils/year. Steam-coil temperatures were estimated to be about 125°C. Corrosion of the steam coils, measured as loss of weight, occurred as general intergranular attack with no selective attack at the walls or at the liquid interface.

Corrosion of Monel During Dissolution of Zirconium Alloy Fuel

The ICPP is continuing its tests of flow sheets that have potential use in a proposed continuous zirconium dissolution scheme. A welded Monel pilot-plant dissolver was recently inspected after 650 hr in uranium–Zircaloy-2 dissolution service[35] in which 4.8*M* hydrofluoric acid was used for 270 hr and 4.8*M* hydrofluoric acid–0.03*M* nitric acid for 380 hr. The dissolver was cut in half lengthwise, and the walls of both halves were inspected. Localized attack and pitting had occurred at various places on the inside walls of the dissolver. Pits up to 20 mils deep were present midway up the dissolution section, presumably at the location where the most vigorous dissolution occurred. Pits less than 5 mils deep were present in the vapor space where the fuel enters the dissolver. Except for these localized sites, pitting and general corrosion were absent.

Resistance of Corronel 230 to Corrosion

Corronel 230* is an alloy developed by a British firm, presumably for the specific purpose of resisting nitric acid–hydrofluoric acid mixtures. The ICPP and ORNL have been testing this alloy with various acid mixtures of interest.[35,40,41] Some of the more pertinent results for this alloy, together with comparative

*Nominal composition: 65% nickel and 35% chromium; obtained from International Nickel Company; produced by Henry Wiggins, Ltd., Birmingham, England.

results for stainless-steel type 309SCb, Hastelloy F, and Titanium-45A, are included in Table II-3. All boiling mixtures containing 10*M* nitric acid (with fluoride contents of 0.5*M* to 5.0*M*) but no aluminum nitrate corroded Corronel 230 at the unacceptably high rates of in solution corrosion rates in excess of 20 mils/month. The addition of hydrogen peroxide to the extent of 0.1*M* decreased the solution corrosion rate to less than 3 mils/month but increased the attack in the vapor phase from 4 to 15 mils/month.

Table II-3 ALLOY CORROSION IN NITRIC-HYDROFLUORIC ACID MIXTURES[35,40]

(Temperature: Boiling)

Alloy	Time, hr	Solution composition			Corrosion rate, mils/month
		HNO_3, moles/liter	HF, moles/liter	$Al(NO_3)_3$, moles/liter	
Corronel 230	4	1.0	1.0		Dissolved
Corronel 230	257	4.0	0.3		2.1
Corronel 230	103	4.0	5.0		63
Corronel 230	96	10.0	0.5		60
Corronel 230	103	10.0	1.0		56
Corronel 230	89	10.0	5.0		170
Corronel 230*	48	6.0	1.0		47
Corronel 230*	20	0.25	6.0		540
Corronel 230	408	10.0	0.5	0.75	0.7
Stainless steel 309SCb	36	10.0	0.5		212
Hastelloy F	8	10.0	0.5		260
Titanium-45A	408	10.0	0.5	0.75	0.3

*Data are from Ref. 35. All other data are from Ref. 40.

greater than 50 mils/month. Aluminum nitrate added to the extent of 0.75*M* was an effective inhibitor and reduced the corrosion rate to 0.7 mil/month. Without inhibitor addition, corrosion rates could be reduced only by decreasing the concentration of both acids. Despite its poor resistance to corrosion, Corronel 230 was superior to either stainless-steel type 309SCb or Hastelloy F. With inhibitor added, Corronel 230 is nearly competitive with titanium. Decreasing the nitric acid and hydrofluoric acid concentrations to 1.0*M* and 3.0*M*, respectively, and lowering the temperature to 60°C reduced the corrosion rates of Corronel 230 to less than 1 mil/month. Although this drastic change of environmental conditions produces lowered corrosion rates, operation at such a low temperature is not likely to be applicable to any practical process. Both ICPP and ORNL have concluded that this alloy is not suitable for most applications utilizing these acid mixtures.

The corrosion of Corronel 230 is being determined in typical Perflex-process environments (1*M* hydrofluoric acid–0.06*M* hydrogen peroxide).[40,42] Exposure to refluxing, nonperoxide-containing 1*M* hydrofluoric acid resulted

Resistance of Aluminum Alloy to Nitric-Hydrofluoric Acid Solutions

Boiling strong nitric acid (up to 23*M*) containing up to 3*M* hydrofluoric acid is being considered as a dissolution medium for graphite and carbide-containing fuels. In recent corrosion work the behavior of aluminum alloys (types 1100 and 6061) as construction materials has been compared with the behavior of austenitic stainless steels.[40,41] The successful passivation of aluminum by these strong nitric acid environments is indicated by the results shown in Table II-4. Type 6061 aluminum appears to be competitive with stainless-steel types 309SCb and 347. It possesses the advantage that activation of the metal does not occur in the presence of graphite and uranium, as had been previously observed with stainless-steel type 309SCb. Lowering the temperature of the 14*M* nitric acid medium was found to increase rather than decrease the corrosion rate of aluminum.

Resistance of Titanium to Corrosion

The corrosion characteristics of Darex-process solutions for the dissolution of stain-

Table II-4 CORROSION OF ALUMINUM ALLOY AND STAINLESS STEEL IN REFLUXING HNO_3-HF SOLUTIONS[40,41]

Alloy	Time, hr	Solution composition		Corrosion rate, mils/month		
		HNO_3, moles/liter	HF, moles/liter	In vapor	At interface	In solutions
6061 aluminum	144	23	1	0.1	Gain	Gain
6061 aluminum	96	14	1	0.5	Gain	0.1
6061 aluminum	96	14	3	4.7	2.5	4.0
Stainless steel 309SCb	144	23	1	<0.1	0.6	0.3
Stainless steel 347	96	22	2	0.1	0.5	0.5

less-steel matrix fuels have been explored rather thoroughly in the past, and titanium appears to be by far the best construction material available. Recent supplemental corrosion studies were made (1) to determine the effect on corrosion of the presence of fluoride in Darex-process dissolver solutions, (2) to determine whether the usual dissolvent for aluminum fuels (nitric acid containing mercuric nitrate) is compatible with titanium equipment, and (3) to determine whether the dissolvent for uranium-molybdenum fuels (nitric acid containing ferric nitrate) is compatible with titanium equipment. In the latter two environments (refluxing), titanium corroded at rates of less than 1 mil/month in exposures of 500 to 1000 hr; this is considered acceptable. In the first environment, addition of up to 0.04*M* fluoride has been shown to transform silica in the dissolved stainless-steel solutions from a troublesome gel to a granular form that can be readily handled. Since borate might also be present for criticality control, and aluminum or zirconium might be introduced as a corrosion inhibitor, these materials were also present in the tests that were made. Results are shown in Table II-5. The amount of boron in the form of fluoboric acid was found unexpectedly to have a pronounced adverse corrosion effect. On the basis of these results, Oak Ridge concluded that the proposed addition of fluoride is not compatible with titanium equipment in the Darex process.[43]

Corrosion in Sulfex- and Zirflex-Process Media

Corrosion tests have been continuing at Brookhaven National Laboratory (BNL) on the alloy Nionel in Sulfex-process media.[44] Results indicate that Nionel is a satisfactory material for use in 4*M* H_2SO_4, in both the liquid and vapor phases, and also for heat-transfer surfaces, but long-term tests in 6*M* H_2SO_4 have shown progressively increasing rates of attack. Tests in nitric acid have shown severe intergranular attack on vapor-phase specimens above 8*M* and 10*M* HNO_3. Tests with refluxing 5*M* and 6*M*

Table II-5 CORROSION OF WELDED SPECIMENS OF TITANIUM-45A IN INITIAL DAREX SOLUTIONS[43] AT 87°C

Test period, hr	Solution composition	Condenser			
		Condenser	Vapor	Interface	Solution
24	1*	<0.1, 0.1	3.1, 2.7	41.0, 42.8	76.2, 74.9
	2†	0.1, <0.1	1.6, 1.0	30.0, 32.7	59.1, 60.5
48	1	<0.1, <0.1	2.0, 2.3	46.8, 45.9	82.5, 81.3
	2	<0.1, <0.1	1.2, 1.1	31.6, 35.6	62.3, 60.9
72	3‡	<0.1, <0.1	0.6, 1.2	10.6, 12.3	15.6, 15.3
168	3	<0.1, <0.1	0.9, 0.8	8.6, 11.6	7.5, 7.3

*Solution composition: 5*M* HNO_3 – 2*M* HCl – 0.005*M* $Na_2B_4O_7$ – 0.01*M* HBF_4 – 0.01*M* $ZrO(NO_3)_2$.

†Solution composition: 5*M* HNO_3 – 2*M* HCl – 0.005*M* $Na_2B_4O_7$ – 0.01*M* HBF_4 – 0.04*M* $Al(NO_3)_3$.

‡Solution composition: 5*M* HNO_3 – 2*M* HCl – 0.0025*M* $Na_2B_4O_7$ – 0.01*M* HBF_4 – 0.04*M* $Al(NO_3)_3$.

HNO_3 have shown gradually increasing corrosion rates of vapor-phase specimens, reaching about 24 mils/year after 1680 hr. Tests with Nionel heat-transfer surfaces in boiling nitric acid have shown severe intergranular attack under all conditions tested. Tests in progress indicate that satisfactory corrosion rates may be realized on heat-transfer surfaces if the solution is maintained below the boiling point.

The corrosion of Nionel in nitric acid vapor is also being examined at ORNL for possible application in the Sulfex and Zirflex processes.[40] The corrosion rate increased rapidly with increasing concentration of nitric acid. For 360-hr exposures the rates of attack of vapor specimens above 4*M* and 15.6*M* nitric acid were 0.3 and 37 mils/month, respectively. Grain-boundary attack was observed in every case and developed into aggressive intergranular attack at the higher HNO_3 concentrations. Oak Ridge indicates that these results represent maximum rates; the effect of Sulfex or Zirflex dissolution cycles would probably be to delay the onset of aggressive intergranular attack.

Corrosion studies of Nionel and 309SCb and 304L stainless steels in Zirflex solutions have continued at BNL.[44] None of these materials is satisfactory in noninhibited boiling Zirflex solutions (ammonium fluoride–ammonium nitrate). Only 309SCb shows promise in boiling solutions containing 0.01*M* Cu^{2+} as an inhibitor. However, the copper slowly plates out on the specimen, and the corrosion rate increases with loss of inhibitor from solution. Recent tests at 90°C have shown that 309SCb is satisfactory for use with Zirflex solutions, even without an inhibitor. Corrosion of 304L in noninhibited Zirflex solutions is markedly decreased at 90°C but still is not satisfactory. However, satisfactory rates are achieved using 0.01*M* Cu^{2+} as an inhibitor. Under these conditions there is no evidence of loss of inhibitor as was observed in boiling solutions.

Miscellaneous Corrosion Information

Hanford is contemplating the use of boron-containing stainless steels or Pyrex Raschig rings (containing boron) for criticality control in nitric acid process environments. When exposed to 60% nitric acid at 50°C, stainless-steel type 304 containing 1 wt.% boron corroded at rates of less than 0.05 mil/month.[45] Pyrex Raschig rings exposed to 13*M* nitric acid–1.0*M* hydrofluoric acid at room temperature corroded at a rate of about 100 mils/month. The corrosion rate of both materials was less than 0.05 mil/month in 2*M* nitric acid containing 1.25*M* aluminum nitrate and 0.25*M* hydrofluoric acid.

In tests conducted at Hanford, samples of Rigimesh stainless-steel type 304 wire filters were vacuum annealed and air-cooled in an attempt to decrease corrosion by nitric acid. Exposure of the annealed samples to boiling 65 wt.% nitric acid for 120 hr caused the smallest wires to corrode to about one-half of their original thickness. This represents a substantial improvement over unannealed material.[46]

An eight-volume bibliography on nuclear reactor fuel processing and waste disposal has been published.[47] A total of 26 pages of Vol. V is concerned with corrosion and with construction material problems.

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Liquid-Phase Processes

Nitrofluor Process. The initial step in the Nitrofluor process, under development at Brookhaven National Laboratory (BNL), is the dissolution of reactor fuel assemblies in an anhydrous NO_2-HF solution. A solution that contains 20 mole % NO_2 is capable of dissolving a wide variety of fuel-element materials at satisfactory rates over a temperature range of 100 to 200°C. After dissolution of the fuel elements, uranium and plutonium are recovered as volatile hexafluorides. The high reactivity of the solvent has limited the choice of container materials to Monel and nickel. These materials, however, do experience corrosion during the solvent evaporation and condensation steps. Oxidizing agents such as molecular nitric acid or the nitryl ion (NO_2^+) are believed to be responsible for the attack on Monel and nickel.

Two alternative solvents, NOF·3HF and N_2O_3-HF, are presently being evaluated since they do not possess the oxidizing characteristics of the NO_2-HF solvent. Both solvents are capable of dissolving zirconium, aluminum, UO_2 ceramic fuel, and type 304 stainless steel at satisfactory rates.[1] Thus the versatility of these solvents approaches that of NO_2-HF, the essential difference being that they do not disintegrate graphite or graphite-matrix fuels. This difference in behavior is believed to be due to the action of nitryl ions or molecular nitric acid on the graphite. Confirmation of this phenomenon was established in a test[1] in which a graphite sample was completely disintegrated by 100% nitric acid.

The Nitrofluor solvents react with fuel materials to form nitrosyl metal fluoride complex salts which have a low solubility in the solvents.[1,2] The complex salt produced by dissolution of uranium metal or oxide in the solvents has been identified as nitrosylium hexafluorouranate ($NOUF_6$). In the processing of high-zirconium alloy fuels containing enriched uranium, the bulk of the zirconium precipitates as an insoluble complex salt. Since the concentration of uranium does not exceed the solubility of $NOUF_6$, the uranium remains in solution. One method that was tested for recovering uranium from the two-phase dissolution product involves evaporation of the dissolver solution followed by fluorination of the residue with bromine trifluoride to form volatile uranium hexafluoride. After six treatments with bromine trifluoride at 150°C, the nonvolatile uranium in the zirconium salt was reduced to 94 ppm, equivalent to a uranium recovery[1] of 99.8%.

An alternative technique has been developed[1,2] for separating uranium from solid $NOUF_6$. The method involves contacting the solid with either gaseous NOF·3HF or NOF at 400 to 500°C to form a volatile uranium compound. Complete uranium volatilization from $NOUF_6$ has been demonstrated in laboratory tests. Uranium tetrafluoride has been identified as one of the solids that condensed in a downstream zone at 400°C. Although the reactions are not yet understood, this method appears to have direct application to the Nitrofluor process. Thus NOF·3HF could serve initially as the fuel solvent and subsequently as the volatilizing agent.

Several tests have been performed to evaluate the behavior of nickel exposed to NO_2-HF solutions during Zircaloy-2 dissolution and during condensation of the evaporated dissolver solution.[1] High-purity nickel (Nickel 270) was compared with commercially pure nickel (Nickel 200) for several solvent-to-dissolved-metal

ratios. These tests showed that Nickel 200 corrosion in this system can be significantly reduced by increasing the solvent-to-dissolved-metal ratio. Under the more severe corrosive conditions, Nickel 270 was consistently superior to Nickel 200.

Significant progress has been made in solving the corrosion problem associated with handling the three Nitrofluor solvents in nickel or Monel equipment. A series of tests was made in which Monel alloy 400 was compared with Nickel 200 in each of the three solvents in the presence of (1) dissolved zirconium and (2) dissolved uranium dioxide with type 304 stainless steel.[1] The results showed that zirconium-matrix fuel was best handled in Nickel 200 equipment using $NOF \cdot 3HF$ as the solvent. The best combinations for uranium dioxide fuel appeared to be Nickel 200 as the construction material with NO_2-HF as the solvent, and Monel alloy 400 with $NOF \cdot 3HF$ as the solvent. If both zirconium and uranium dioxide fuels are to be processed in the same equipment, Nickel 200 would be the preferred construction material.

Fused-Salt Volatility Process

The fused-salt fluoride-volatility process being developed at Oak Ridge National Laboratory (ORNL) for uranium recovery utilizes dissolution of fuel by hydrofluorination followed by direct fluorination of uranium to the hexafluoride which volatilizes. Both these steps are carried out in the presence of a molten fluoride salt at temperatures of 500 to 600°C. Next, absorption and desorption of the uranium hexafluoride on sodium fluoride beds effects high decontamination from fission products and impurities. Considerable work has been done on these process steps, but this work has been limited to fuels containing only uranium as the fissionable constituent.

Recently, exploratory work has been reported by Cathers and Jolley of ORNL[3] on the volatilization of plutonium hexafluoride from fused salts with fluorine. Some tests with solid absorbents were also carried out. These tests were made at 600°C in 50-50 mole % NaF-ZrF_4 or in 31-24-45 mole % LiF-NaF-ZrF_4 fused salt, with initial plutonium concentrations of 2 ppm in the salt. Although only 0.1 mc of Pu^{239} was used in each test, the recoveries and material balances were good.

The rate of removal of plutonium from the salt by fluorination appeared to follow the relation

$$\frac{d \ln C}{dt} \propto G$$

where C is the concentration of plutonium in the salt, t is the time, and G is the rate of fluorine gas flow. Removal half times of about 3 hr were obtained in the 1-in.-diameter fluorinator at 100 to 150 ml of fluorine per minute.

The absorption behavior of the plutonium fluorination product was examined by passing the fluorination effluent gas through packed beds of sodium fluoride, lithium fluoride, and calcium fluoride. Experiments were performed in which uranium hexafluoride–plutonium hexafluoride was used, in order to get information on absorption as a separation method. The results on the retention of plutonium and uranium on these beds can be summarized as follows:

	Retention on bed material					
	25 to 100°C			400°C		
	NaF	LiF	CaF_2	NaF	LiF	CaF_2
Pu	Yes	Yes*	Yes	Yes†	No*	Yes†
U	Yes‡	No	No	No	No	No

*Absorption appears reversible.
†Absorption appears irreversible.
‡Absorption completely reversible.

The data indicate that any of these fluorides may be used to remove plutonium hexafluoride selectively from a gas stream in the presence of uranium hexafluoride. Lithium fluoride may be especially useful in that the plutonium absorption appears to be reversible.

Dry Halogenation Processes

Several processes that involve separation methods based on the relative volatility of the chlorides are being developed for processing of reactor fuel elements. Engineering-scale studies are continuing at Argonne National Laboratory (ANL) on a process for the recovery of highly enriched uranium from zirconium alloy fuels. The process is based on the use of hydrogen chloride, at a temperature of 400°C, to convert zirconium-uranium alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. Recovery of uranium values is achieved by the reaction between uranium tri-

chloride and fluorine at 400 to 500°C to produce volatile uranium hexafluoride. Both reactions are conducted in a fluidized bed of inert Alundum particles. Fluidized beds offer the advantage of permitting the highly exothermic reactions to be carried out under nearly isothermal conditions.

Process studies are being conducted in a $1\frac{1}{2}$-in.-diameter fluid-bed reactor. Since a portion of the uranium trichloride particulate solids is entrained in the off-gas stream from the fluid-bed reactor during hydrochlorination, a static-bed gas filter consisting of alternate layers of coarse and fine Alundum particles has been installed in series with the reactor to ensure uranium retention within the system. Recent studies[4] have been concerned with the effect of several chlorination-fluorination cycles on overall uranium recovery. Two cycles were evaluated: (1) hydrogen chloride followed by phosgene and then fluorine and (2) 4 : 1 mixture of hydrogen chloride and phosgene followed by phosgene and then fluorine. Greater losses of uranium through the static-bed filter were sustained when a hydrogen chloride–phosgene mixture was employed than with hydrogen chloride alone. In tests employing the use of phosgene, the residual uranium concentration in the Alundum bed after fluorination was, in general, only slightly less than when hydrogen chloride alone was used. It appears that the results obtained do not warrant the use of phosgene in the process scheme.

The volatile zirconium tetrachloride produced during hydrochlorination of uranium-zirconium alloy fuel represents a waste stream that requires processing for convenient storage. Zirconium tetrachloride is rapidly converted to solid zirconium dioxide by a gas-phase reaction with steam. Process studies are being made[3] to demonstrate this reaction in a 6-in.-diameter fluid-bed system. The gas stream, containing zirconium tetrachloride diluted with nitrogen, is fed directly into a heated (350°C) bed of zirconium dioxide. This gas stream serves as the fluidizing medium. Steam is introduced into the system at a point about 11 in. above the gas distributor plate, at a rate approximately three times the stoichiometric requirement.

Current studies have been directed toward establishing process conditions that will promote efficient deposition of the zirconium dioxide product on the surface of the bed particles and, at the same time, allow operation at high zirconium tetrachloride feed rates. Successful operation has been demonstrated with $ZrCl_4$ feed rates up to 3.3 kg/hr. Although a significant portion of the zirconium dioxide is produced in the form of fines (up to 27% of the product is −200 mesh), operation of the reactor has been trouble-free in runs up to 6 hr in duration. Lowering the bed temperature to 250°C had no effect on the quantity of fines in the product. Similarly, the use of a starting bed of zirconium dioxide containing primarily coarse particles did not diminish the quantity of fines produced.

Processes Based on Uranium Chlorides

J. Schmets and associates at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium, are developing a method for processing irradiated uranium and uranium compounds based on the fractional sublimation of chlorides. Recent work[5,6] has concerned the study of the reaction between uranium dioxide and various chlorinating agents. Uranium dioxide fuels are oxidized to U_3O_8 and then reduced to the dioxide to obtain a fine powder highly reactive toward chlorination. Both hydrogen and carbon monoxide are being considered as reducing agents,[5] with carbon monoxide apparently preferable because no water is produced when it is used. The reactive uranium dioxide is converted to uranium tetrachloride by a gas-phase reaction with carbon tetrachloride. Previous work[7] has shown that, to obtain a pure uranium tetrachloride product, it is necessary to add a reducing agent to the carbon tetrachloride. Without this precaution, a relatively high proportion of volatile uranium chlorides (UCl_5 and UCl_6) are formed. Chloroform has been found[5] to be an effective agent in converting uranium dioxide to uranium tetrachloride. Uranium dioxide reacts rapidly with chloroform at 450°C, producing uranium tetrachloride. At higher reaction temperatures some carbon appears in the product.

One aspect of this investigation has been to determine if various fission-product materials can be separated from uranium during chlorination. Niobium oxide is converted to a volatile chloride in chloroform at temperatures above 350°C. Attempts to separate uranium from a UO_2-Nb_2O_5 mixture by reaction with chloroform have given nonreproducible results. Separation of niobium from uranium tetrachloride may be

effected by oxidation of the chlorides in dry air at 500°C. A volatile niobium chloride ($NbOCl_3$) is produced which readily separates from uranium tetrachloride.

In the processing of certain reactor fuels, it may be advisable to convert the uranium initially to volatile chlorides (UCl_5 and UCl_6) to achieve preliminary decontamination. Final decontamination could be effected by the conversion of the volatile chlorides to uranium hexafluoride. Since there was considerable uncertainty concerning the nature of the products of the reaction between uranium hexachloride and hydrogen fluoride, a comprehensive study has been made[6] to determine under what conditions, if any, uranium hexafluoride may be prepared by this reaction. The reaction between a mixture of UCl_5 and UCl_6 and hydrogen fluoride was investigated over the temperature range of 120 to 300°C. In all tests the product of the reaction was a mixture of uranium pentafluoride and uranium tetrafluoride; in no case was any uranium hexafluoride produced. Similar tests[6] showed that the reaction between uranium trichloride and hydrogen fluoride produced uranium tetrafluoride rather than the trifluoride.

Direct Fluorination Processes

A direct fluorination volatility process is being developed at ANL[4] to recover uranium and plutonium from spent uranium oxide fuel elements that are clad with Zircaloy or stainless steel. The proposed process for recovery of uranium and plutonium from spent fuel involves decladding by an appropriate reaction in a fluidized bed. Plutonium hexafluoride and uranium hexafluoride, which are formed upon the reaction of the declad oxide fuel with fluorine, may be separated from volatile fission products by distillation and then may be separated from one another by thermal decomposition of plutonium hexafluoride.

Direct Fluorination of Uranium Dioxide Pellets. The direct fluorination of uranium dioxide pellet fuel is being studied[4] on an engineering scale in a 3-in.-diameter air-cooled reactor with the aim of optimizing reaction rate, fluorine efficiency, and fluidization quality. The reaction is carried out in a fluidized bed in which pellets of uranium dioxide form a packed bed, with fluidization provided by means of inert granular solid in the space above and in the voids of the pellet bed. The fluidization aids in the heat transfer and in the mixing of solid fines formed as intermediates during the reaction. Oxygen added as a component of the fluorinating gas influences the reaction behavior by the formation of U_3O_8 fines.

A series of tests was performed to evaluate the effect of fluidizing gas rate on uranium hexafluoride production rate.[4] Whole pellets were added to the reactor at 1-hr intervals to maintain a constant pellet-bed height of 6 in. and to approximate more closely steady-state conditions. Fluorination was carried out with 10% F_2–90% N_2 gas at 500°C at fluidizing gas rates between 0.5 and 1.3 ft/sec. It was observed that the uranium hexafluoride production rate increased only about 40% for a gas rate increase of 170%. Because gas rate had only a slight effect, the fluorine utilization efficiency was 24.5% at the lower fluidizing gas rate and 17.5% at the higher gas rate.

The effect on uranium hexafluoride production rate of oxygen concentrations of 5 and 13%

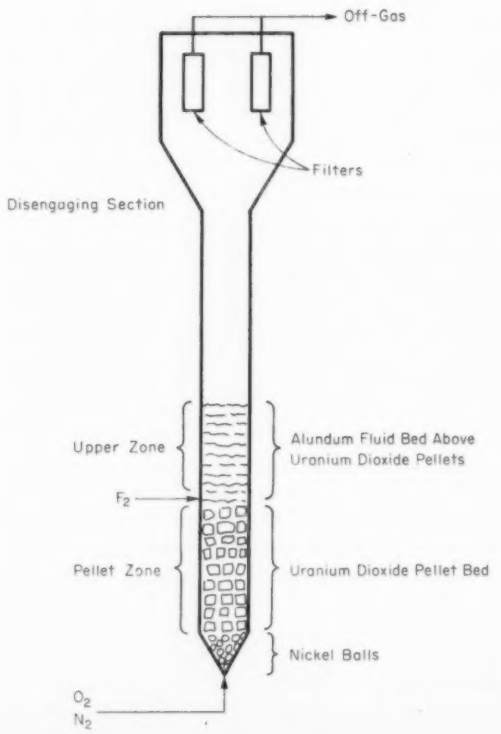

Fig. III-1 Schematic diagram of fluorinator in two-zone operation.[4]

in the fluidizing gas was studied in additional tests.[4] Satisfactory fluidization quality was achieved in a test with the lower oxygen concentration but not in the case with 13% oxygen. With 5% oxygen in the fluidizing gas, the steady-state production rate was 40 lb of UF_6/(hr)(sq ft of reactor cross section), and the fluorine utilization efficiency was 56%.

An analysis was made of the factors that tend to produce conditions of poor fluidization. On the basis of the results of this analysis, a two-zone scheme was proposed. In this scheme a mixture of oxygen and nitrogen is introduced into the lower zone, which contains the bed of uranium dioxide pellets, and fluorine is introduced into the upper zone, which consists of a fluidized bed of Alundum particles (Fig. III-1). Uranium oxide fines (U_3O_8) are formed in the lower zone and elutriated into the upper zone where they are fluorinated, forming volatile UF_6. One advantage of this scheme is that the possibility of caking (due to reactions of uranium hexafluoride with uranium oxides which lead to the formation of solids) may be minimized. Also, in the two-zone scheme, heat removal is more favorable than in the one-zone scheme employed previously. This arises from the fact that only the oxidation reaction ($\triangle H = -26$ kcal/gram mole of uranium at 25°C) takes place in the pellet bed, whereas fluorination of the fines ($\triangle H = -231$ kcal/gram mole of uranium at 25°C) takes place in the upper unhindered fluidized bed of Alundum.

In an initial batch run carried out with a 12-in.-deep pellet bed at 500°C, good fluidization quality was achieved. The gas rate in the pellet zone was 1.2 ft/sec, and the oxygen concentration was 4 to 8%. Fluorine concentration in the gas in the upper zone was varied from 5 to 13%. The overall uranium hexafluoride production rate was 33 lb of UF_6/(hr)(sq ft), and the overall fluorine utilization efficiency was 61%.

Thermal Decomposition of Plutonium Hexafluoride. Selective thermal decomposition of plutonium hexafluoride is being considered as a means of separating the mixture of uranium hexafluoride and plutonium hexafluoride produced in the fluorination of uranium dioxide fuel. It has been demonstrated[4] that circulation of gaseous mixtures of uranium hexafluoride and plutonium hexafluoride through nickel vessels containing nickel wool and plutonium tetrafluoride at 200 to 300°C reduces the ratio of plutonium to uranium by factors between 10^2 and 10^3 as a result of decomposition of PuF_6 to PuF_4.

The best separation was obtained at 200°C when a mixture of gaseous hexafluorides with an initial ratio of uranium to plutonium of 12.8 was circulated through the decomposition vessel for 10 hr. This was equivalent to a residence time in the decomposition vessel of 6.6 min for the entire mixture. The ratio increased to 1.94×10^4, indicating a removal of 99.9% of the initial plutonium from the gas. At 300°C the maximum ratio of uranium to plutonium was reached much more rapidly. During a circulation time of $1\frac{1}{3}$ hr (residence time 0.88 min) through a vessel at 300°C, the uranium-to-plutonium ratio of a gas mixture was increased from 9.88 to 3.48×10^3, indicating a removal of 99.7% of the initial plutonium from the gas.

The extent of separation at equilibrium decreases as the temperature of the vessel increases. This relation is expected because the equilibrium constant, $[PuF_6]/[F_2]$, for the reaction $PuF_4(s) + F_2(g) \rightarrow PuF_6(g)$ increases with temperature. The rate of separation increases with temperature since the rate of decomposition of plutonium hexafluoride vapor increases with temperature.

The percentage of uranium in the deposited plutonium tetrafluoride increased with the residence time of the gas mixture in the hot vessel. The purest plutonium tetrafluoride product was obtained in a test in which a gas mixture with an initial concentration of 90.8% UF_6 and 9.2% PuF_6 in total hexafluorides was circulated through a vessel for $1\frac{1}{3}$ hr (residence time in vessel 0.88 min) to deposit plutonium tetrafluoride that had a uranium content of 0.091%.

It appears that thermal decomposition can be used to separate plutonium hexafluoride from uranium hexafluoride at rates that are practical for application to the fluoride-volatility processing of power-reactor fuels.

Decomposition of Plutonium Hexafluoride by Radiation. During the fluorination step and in subsequent operations, plutonium compounds are exposed to radiation from fission products. A study[4] of the decomposition of plutonium hexafluoride by gamma radiation has been undertaken to obtain information concerning the extent of decomposition, the products of the decomposition, and the fundamental processes

involved in the radiation chemistry of plutonium hexafluoride. Data obtained show an increase of the extent of decomposition with increasing amounts of energy absorbed in plutonium hexafluoride. Plutonium tetrafluoride and fluorine were identified as the products of the decomposition. The *G* value for the decomposition is 7 molecules of plutonium hexafluoride decomposed per 100 ev absorbed.

G values obtained in experiments using helium as a diluent for PuF_6 were compared with those obtained in experiments carried out in the absence of helium. Helium was found to have no appreciable effect on the decomposition. This may be attributed to the small contribution of helium to the total electron density of the mixture, coupled with the high ionization potential and the high energy of the first electronic excited state of helium, resulting in an improbable energy transfer between plutonium hexafluoride and helium. Krypton, however, appears to enhance slightly the gamma decomposition of plutonium hexafluoride, whereas oxygen appears to depress the decomposition.

Plutonium hexafluoride has been synthesized by the action of gamma radiation on mixtures of plutonium tetrafluoride and fluorine.[4] The product was identified by its infrared spectrum and its vapor pressure. The quantities of plutonium hexafluoride produced were greater than those expected from knowledge of the thermodynamic equilibrium constant.

Filtration of Hydrolyzed Plutonium Hexafluoride. Glove-box enclosures that are used for the handling of plutonium hexafluoride have filters attached to the inlet and outlet of the ventilation system of the enclosures to prevent the discharge of plutonium particulate matter. Since plutonium hexafluoride will react rapidly with water vapor present in the glove-box atmosphere, an investigation was made[4] of the factors that will affect the filtration of plutonium particulate matter obtained through the hydrolysis of plutonium hexafluoride. The filters evaluated were AEC type filters used in most glove-box installations.

Particulate penetration data were obtained from experiments in which small-scale releases of plutonium hexafluoride, 25 mg or less, were made into an atmosphere of known moisture content. The resulting air mixtures were passed through AEC filters, a water bubbler, and Millipore filters in a series, at a controlled flow rate. Gamma and/or alpha counts of the filters and bubblers were used to determine penetration for individual filters and for combinations of filters.

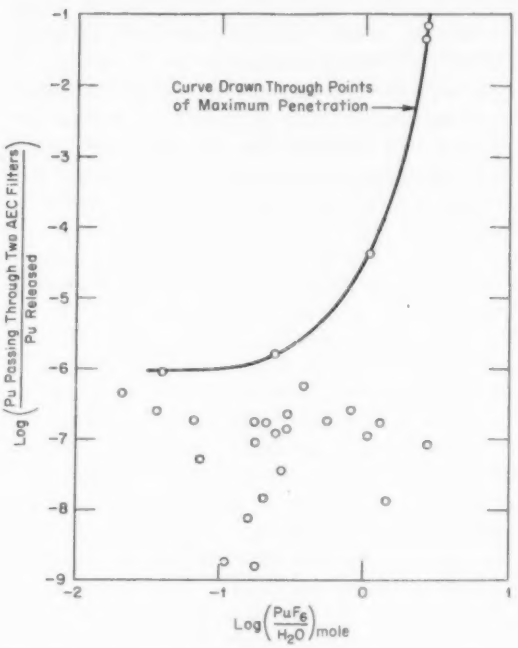

Fig. III-2 Fraction of released plutonium hexafluoride passing through two AEC filters.[4]

In Fig. III-2 the logarithm of the ratio of plutonium passing through two AEC filters to the plutonium released is plotted against the logarithm of the ratio of moles of PuF_6 to moles of H_2O initially present in the mixing chamber. The amount of PuF_6 released varied between 1.5 and 25 mg. The moisture content of the air varied between 0.9 and 11 mg of water per liter of air. In all tests the air velocity through the filters was 1.0 cm/sec. When there was sufficient moisture in the air to hydrolyze completely the PuF_6 released, the penetration of two AEC filters in series varied from 1 part per million parts released to 2 ppb. Some of the scatter of the data may be attributed to the variation of turbulent flow in the mixing chamber, variation in different samples of filter media, and variation in particle agglomeration.

Most of the hydrolyzed plutonium hexafluoride was found by microscopic examination to

be in the form of agglomerates. The agglomerates observed had a wide size range and were composed of spherical particles from 0.01 to 0.2 μ in diameter.

The extrapolation of information obtained in these experiments to the filter systems of glove-box facilities used at ANL for handling of plutonium hexafluoride indicates that the installations can safely handle up to 50 g of PuF_6 when the partial pressure of water in the glove-box air is greater than 6.8 mm Hg. This partial pressure of water is equivalent to a relative humidity of 40% at 67°F. Since the atmospheric water content may decrease to as low as 0.3 mm Hg, humidification of the glove-box atmosphere may be necessary at times.

Preparation of Fuels for Volatility Processing. Schmets and associates at CEN[5,6] (Mol, Belgium) are developing a fluorination process for the recovery of uranium from sintered uranium oxide fuel. To minimize fluorine requirements, the oxide fuel is initially converted to uranium tetrafluoride. The sintered oxide is activated by an oxidation-reduction procedure prior to conversion to UF_4 with hydrogen fluoride. Oxidation is carried out[6] by reaction with air at 450°C. Reduction of the U_3O_8 fines is then accomplished by the use of 25 vol.% hydrogen in nitrogen at 500°C. This oxidation-reduction cycle effects an appreciable increase in hydrofluorination rate in comparison to the sintered pellets.

The direct conversion of uranium monocarbide to uranium tetrafluoride with hydrogen fluoride appears to be a promising method for carbide fuel processing. Unlike sintered uranium dioxide, sintered pellets of uranium carbide are readily reacted with either liquid[6] or gaseous[5] hydrogen fluoride.

In the reaction between uranium monocarbide and liquid hydrogen fluoride, hydrogen and methane are the primary gaseous products.[6] Saturated hydrocarbons heavier than methane are also formed in proportions that decrease with increases in their molecular weights. The free carbon content of the uranium tetrafluoride product varies from 0.24 to 0.81%, whereas the total carbon content varies from 0.48 to 1.78%, indicating that some saturated hydrocarbons are associated with the UF_4 product.

The reaction of gaseous hydrogen fluoride and uranium monocarbide has been studied[5] in the temperature range of 50 to 450°C. At low temperatures the quantity of hydrogen formed diminishes as the reaction progresses, whereas the quantity of methane and ethane produced increases. The inverse occurs at higher reaction temperature. There appears to be no relation between the temperature of the reaction and the amount of elemental carbon formed.

An alternative approach for processing power-reactor fuels, being studied at CEN,[5,6] involves the oxidation of the fuel, or an intermediate compound, to uranium trioxide prior to fluorination with sulfur tetrafluoride to form uranium hexafluoride. Several tests have been made[5] to evaluate the oxidation of UF_4, UC, and UO_2 in HNO_3 vapor. In the oxidation of UF_4 at 375°C, the yield of UO_3 varied from 98 to 99.7% in tests of 1.5-hr duration. Exploratory tests have shown[5] that nitrogen dioxide is not an effective oxidizing agent for UF_4 or UC.

Studies have been initiated[6] to obtain data on the decontamination of ruthenium and iodine during nitric acid oxidation of UC, UO_2, and UF_4. Depending on the compound being oxidized, from 80 to 95% of the ruthenium is volatilized during a 5-hr oxidation to uranium trioxide. Iodine decontamination was relatively slight for the three feed materials. However, if uranium monocarbide is the starting material, iodine might be eliminated during the hydrofluorination of the carbide to uranium tetrafluoride.

Pyrometallurgical Processes

Pyrometallurgical processes for recovery of discharged reactor fuel material include processes in which fuel materials are processed directly as metals and those processes in which both metal and ceramic fuel materials are processed in liquid-metal–salt solvent systems. The incentive for development of pyrometallurgical processes stems principally from economies that are expected to be derived from the capability of such processes for handling short-cooled fuels with an attendant reduction of fuel inventories and from avoidance or simplification of chemical conversions. Pyrometallurgical processes are not generally high-decontamination processes, and their development must therefore be accompanied by a parallel development of methods for remote refabrication of reactor fuel elements.

The status of processes for recovery of irradiated reactor fuels was reviewed by Levenson,[8] who discusses the utility of these processes within the context of the overall objective of developing economically acceptable reactor fuel cycles for civilian power reactors.

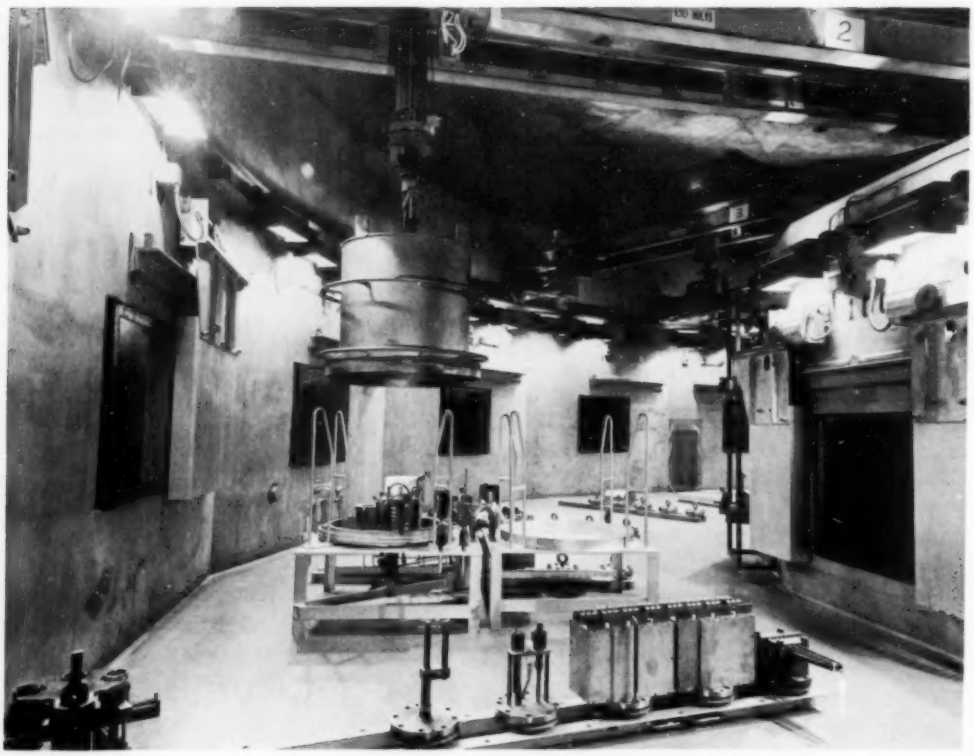

Fig. III-3 Interior of the argon cell of the EBR-II fuel-cycle facility.[9] A melt-refining furnace is shown with its bell-jar cover in the up position. Installation of the furnace was carried out by remote means. In the right foreground a bank of service feedthroughs is seen at floor level. Shown (from left to right) are induction-heating, vacuum, electrical and thermocouple, and pneumatic feedthroughs. In the left foreground a part of a manipulator tool rack and changer is shown. Manipulator bridge cranes span the work area. Two types of steel shielding shutters (to protect the windows from radiation damage when the windows are not in use) are seen hanging from the window shutter rails above the shielding windows. A single type shielding shutter is on the left; a split type shielding shutter is on the right.

Melt Refining

The first reactor-fuel-processing plant based on pyrometallurgical processes will be the fuel-cycle facility that has been constructed adjacent to the Experimental Breeder Reactor No. 2 (EBR-II) at the National Reactor Testing Station (NRTS) in Idaho. Melt refining will be the process employed for purification of the first discharged EBR-II fuel. This is a simple melting process in which fission products are removed from molten uranium at 1400°C by vaporization and by selective oxidation reactions. Figure III-3 is a view inside the argon cell of the EBR-II fuel-cycle facility.[9] A recently installed melt-refining furnace, service feedthroughs, manipulator bridge cranes, and shielding window shutters can be seen.

The behavior of iodine in melt refining is very important since, depending on the amount and nature of iodine in the melt-refining off-gases, measures of various complexities must be taken to reduce the iodine activity in these

off-gases to acceptable levels before disposal to the atmosphere. Chellew's work on iodine behavior in melt refining, which showed that iodine activity was largely deposited on surfaces having temperatures between 450 and 700°C, was mentioned in a previous Review.[10] A similar result was found by Castleman[1,11] at Brookhaven in a program for determining the chemical and physical form in which fission products would be released from a reactor fuel element under accident conditions. Fission-product iodine released from a molten uranium-molybdenum alloy (lightly irradiated) and picked up in flowing helium was found condensed on surfaces at temperatures above 200°C. Both Chellew and Castleman have concluded that iodine released into inert atmospheres exists in a combined form, but the identity of the compound has not been firmly established. When air is present, however, either the iodine is released in elemental form or the element is released from previously deposited iodine compounds on exposure to air. When air was present, most of the iodine was deposited at temperatures below 50°C in cold traps or on charcoal, the latter being effective only for elemental iodine. Castleman also discusses the behavior of other fission-product elements.

The possibility of melt refining under molten oxide fluxes has previously been investigated during development of melt-refining processes.[12–14] When a suitable oxidant is used in the salt flux, rare-earth and alkaline-earth fission-product elements can be selectively oxidized and thereby transferred from the molten-uranium to the molten-salt phase. The possible advantages in using salt fluxes are high product yields, low operating temperatures, and short processing times. However, severe problems were encountered with oxide fluxes. Chief among these were finding combinations of stable oxides with sufficiently low melting points for practical use and finding container materials that are resistant to attack by the molten flux and the molten uranium.

The use of chloride fluxes in melt refining has recently been briefly investigated.[15] Chloride fluxes generally have low melting points (<1000°C), and the container material, beryllia, appears to be highly resistant to attack by chloride fluxes, molten uranium, and two-phase systems of these. As was the case with oxide fluxes, good cerium removal from a uranium-fissium alloy (uranium alloyed with certain fission-product elements, principally molybdenum and ruthenium) was obtained at 1100 to 1300°C using calcium chloride containing a small quantity of uranium tetrachloride or magnesium chloride as an oxidant. With the 700-g charges that were employed, metal ingot yields on pouring at 1300°C were good, varying between 95.7 and 97.6%. Before the metal was poured, the flux was removed by freezing the metal, pouring off the flux, and vaporizing the residual flux under reduced pressure. The applicability of this process to plutonium-containing fuels has not been determined.

Injection Casting of Core I Fuel Rods

After the purification of discharged EBR-II fuel by melt refining, new EBR-II fuel rods are made by injection casting, a process in which the molten fuel alloy is forced by gas pressure into high-silica glass-tube molds. These tubes are later broken away from the cast fuel rods, which are then cropped to length, inspected, and sheathed in stainless-steel cans containing a small amount of sodium as a heat-transfer bond. The details of fabrication of over 11,000 fuel rods for the first core loading (core I) of the EBR-II reactor have been reported.[16]

Properties of Uranium-Fissium Alloy

The properties of uranium-fissium alloys* of the type to be used in the first EBR-II core were previously determined with alloys that did not contain a relatively important constituent, technetium.[17] Since technetium has recently become available in small quantities, the properties of fissium alloys having the full complement of alloying elements has been determined by Bohl and Nevitt.[18] Differences in the behavior of fissium alloys containing technetium and the technetium-free alloys were so minor that the property measurements made on alloys containing no technetium can be reliably applied to technetium-containing alloys. The uranium-technetium phase diagram has been reported by Larsen at Ames Laboratory.[19]

*These are alloys that contain fission-product elements as alloying elements, generally in expected equilibrium concentrations. The major elements (present at concentrations of a few percent) are zirconium, molybdenum, technetium, and ruthenium; minor elements (less than 1%) are palladium, rhodium, and niobium.

Container Materials for Molten Uranium

The possibility of containing molten uranium in tantalum crucibles protected from reaction with the uranium by a layer of tantalum monoboride formed on the tantalum has been mentioned previously in these Reviews.[20,21] Jenkins and Keen have attempted to contain the molten two-phase system, uranium and calcium, in tantalum crucibles coated[22] with TaB or TaB_2. Although coated tantalum crucibles lasted longer than uncoated crucibles, the coating broke down upon solidification of the uranium because of bonding of the uranium to the boride coat. It was concluded that boride coatings cannot be recommended for containing molten uranium and calcium.

Work at Mound Laboratory has shown yttrium to be a satisfactory container material for uranium at temperatures[23] up to 1200°C. Yttrium is not, however, a good container material for molten plutonium, which severely attacks it.[23]

Purification by Electron-Beam Melting

The purification of metals during electron-beam melting and the mechanisms of purification are receiving increasing attention. The Bureau of Mines has reported on the purification of hafnium by electron-beam melting.[24] An electron-beam floating-zinc-melting technique has been investigated by Belk in Britain for the purification of refractory metals.[25] Ames Laboratory has reported[19] considerable purification of cerium from oxygen; of thorium from oxygen, hydrogen, and iron; and of yttrium from hydrogen, fluorine, chromium, iron, and silicon (none from oxygen, carbon, or nitrogen) by electron-beam melting.

Development of Liquid-Metal and Salt Processes

Processes that utilize molten metals and salts as solvent media for processing reactor fuel materials are under development at several atomic energy sites. Purification of reactor fuel materials in liquid metals and salts is effected by favorable solubility or concentration differences of product and impurity elements, by selective oxidation and reduction reactions, and by vaporization of volatile species.

The status of processes under development at Ames Laboratory is summarized in a recently issued annual report.[19] These processes have also been described in earlier Reviews.[26–28]

Ames work on the separation of various metals by oxidation-reduction reactions between potassium chloride–lithium chloride salt and zinc metal systems has been discussed in these Reviews.[29,30] A nearly sequential transfer of solutes between phases can be effected. By stepwise additions of zinc chloride, solutes can be transferred from the zinc phase to the salt phase; by stepwise additions of magnesium, solutes can be transferred from the salt to the metal phase. From the data obtained, activity coefficients and activity-coefficient ratios in zinc have been determined. The experimental evidence obtained indicates that thorium and zirconium have a valence of 3 in the salt phase. This work is also summarized in the Ames Laboratory annual report.[31]

For the EBR fuel cycle, liquid-metal–salt processes are being developed at ANL for isolation of plutonium from EBR-II blanket material and for the recovery of fissionable material from melt-refining residues in skull material (flow sheets given in the October 1962 issue of *Reactor Fuel Processing*).[32] These processes have also been discussed in the 1961 annual report[33] of ANL. In recent small-scale demonstration runs of the skull recovery process conducted within an inert-atmosphere glove box, very poor ruthenium removals were realized.[15] (In this step, ruthenium is extracted into zinc from a uranium oxide–halide-flux slurry). This difficulty was attributed to the loss of oxidizing power in the halide-flux phase through elimination of reactions of the flux constituents with air and water which produce chlorine, hydrogen chloride, and oxychlorides. Good extraction of ruthenium was restored by the addition of small percentages of either zinc chloride or moisture to the salt phase.

Work has continued at Argonne on the development of pyrometallurgical processes for plutonium-bearing fuel materials. A critical pyrometallurgical separation for these fuels is the separation of plutonium from rare earths. As previously reported in these Reviews,[34] the distribution coefficients for rare-earth elements and for plutonium (and uranium) between a magnesium chloride salt phase and a magnesium-zinc metal phase differ sufficiently to permit good separation to be achieved in a few countercurrent extraction stages. Recent work has shown that the value of the separation

factor (ratio of the distribution coefficients) is doubled (from 30 to 60) by a decrease in the extraction temperature[15] from 800 to 425°C. An alternative approach for achieving a separation of plutonium from rare earths utilizes the low solubility of plutonium and uranium and the contrasting relatively high solubility of rare-earth elements in calcium-rich zinc solutions to effect a separation of plutonium from rare-earth elements.[15]

A pyrometallurgical process that has been investigated for the separation of uranium from thorium consists of dissolving a thorium-uranium alloy in magnesium in proportions to form a magnesium–40% thorium solution and a uranium precipitate.[35] Various methods are possible for recovering thorium from the magnesium, such as (1) vaporization of the magnesium and (2) precipitation of thorium as the hydride.[36] A method recently investigated by Hanson[37] of Atomics International involves adding the thorium-magnesium alloy to liquid lithium at 500 to 600°C. The magnesium dissolves in the lithium, whereas thorium is precipitated as a finely divided solid. Magnesium concentrations of about 55% were achievable. By filtration through stainless-steel filters, over 99.97% of the thorium was recovered. Because subsequent lithium recovery would be necessary (proposed to be effected by precipitation and filtration of lithium hydride), this procedure appears to be less attractive than direct vaporization of magnesium or precipitation of thorium hydride.

Johnson of Atomics International has reported on the electrodeposition of thorium from a molten LiCl-KCl-$ThCl_4$ bath into a molten zinc cathode.[38] Current efficiencies of 100% were obtained at both a thorium anode and the molten zinc cathode. Stirring of the zinc cathode was found to be necessary. Thorium concentrations of about 15 wt.% in the zinc cathode could be readily obtained.

Electrolysis has been considered by two French investigators for decontamination of irradiated fuels.[39] By means of anodic and cathodic polarization curves, they have shown good separation of uranium and a noble metal (molybdenum).

Processes are under development at ANL for direct reduction of thorium and uranium oxides to the metals by magnesium-zinc alloys in the presence of halide fluxes. Upon reduction, these metals dissolve in the zinc phase, from which they are subsequently recovered by vaporization of the magnesium and zinc. Final thorium concentrations as high as 9% in the metal phase have been realized upon complete reduction of the thorium oxide.[15] Preliminary experiments on the direct reduction of uranium-ore concentrates indicate that silicon is the principal gangue-element impurity appearing in the uranium product.[15] Pretreatments of the ore concentrate with fluorides to remove silicon as the volatile tetrafluoride have shown promise.

Patents

Two patents describing processes of a pyrometallurgical nature have been recorded:

1. A patent awarded to Teitel[40] for a method of recovering uranium from alloys containing aluminum and uranium. The method involves adding magnesium or a magnesium-zinc alloy to the aluminum alloy in order to precipitate an aluminum-uranium intermetallic precipitate, separating the precipitate, and leaching the aluminum from the precipitate with magnesium or zinc.

2. A patent for the removal of fission-product elements from uranium-bismuth alloys by precipitating them from solution with zinc.[41]

Fundamental Studies Relative to Liquid-Metal Process Development

Solubilities in Liquid-Metal Systems

Solubility values for fission-product elements, fissionable elements, and structural elements in liquid-metal solvents are necessary information for the development of liquid-metal processes. The effect of electronegativity on solid and liquid miscibility has recently been discussed by Hume-Rothery.[42]

Among a compilation of papers on rare-earth research[43] is one dealing with the solubility of rare-earth elements in cadmium.[44] Trends in rare-earth solubility behavior are discussed. The equilibrium solid phases were MCd_6 for light rare-earth elements up to samarium and MCd_{11} for heavy rare-earth metals.

Added to the increasing fund of solubility data are the solubilities of beryllium in bismuth (only 1 ppm at 840°C) and columbium in bismuth[1] (about 100 ppm at 840°C). In a study of the effect of alkali metals on the solubility of uranium in bismuth,[45] it was found that small additions of sodium, potassium, and

cesium increased the uranium solubility; a large addition of sodium decreased the solubility. A 45% increase in uranium solubility, the greatest found, was observed at 450°C for a 0.6% potassium concentration. The combined solubility of uranium and thorium in bismuth was determined[46] at 300 and 1000°C. At 1000°C

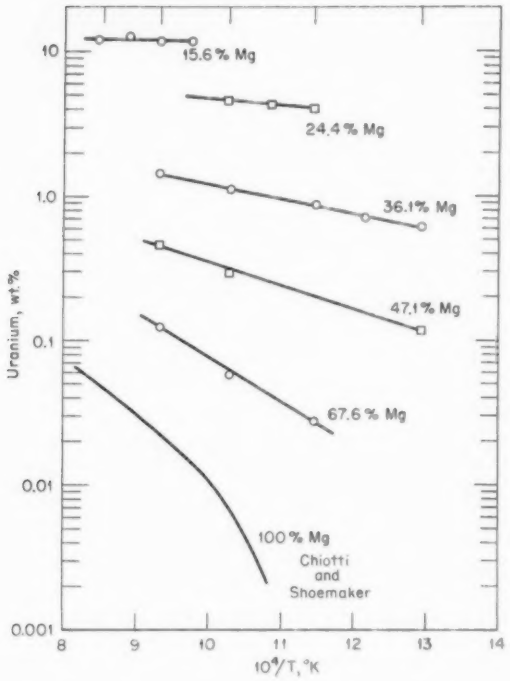

Fig. III-4 The solubility of uranium in zinc-magnesium melts in the temperature and composition range in which the equilibrium solid phase is uranium.[15]

the maximum total solubility was 4.1 at.% thorium and 7.5 at.% uranium. Only a trace of thorium and 0.1 at.% uranium were in solution at 300°C. The solid phases in equilibrium with the liquid were $ThBi_2$ and UBi_2. Considerable information about bismuth has been provided by Fritz in a review publication.[47]

The solubility of technetium in zinc has recently been reported.[15] A minimum in the solubility of the second transition metals in zinc occurs at technetium, confirming a prediction made several years ago.[48,49]

Knowledge of the solubility of uranium in zinc-magnesium alloys is of particular importance in relation to liquid-metal processes now under development at Argonne. As the magnesium concentration in zinc is increased from zero, the uranium solubility first decreases slightly and then increases to a maximum at about 10 wt.% magnesium concentration. Further increase in the magnesium concentration causes a precipitous drop in uranium solubility and is associated with changes in the equilibrium solid phase. Additional solubility measurements in the high-magnesium region have recently been reported[15] and are presented in Fig. III-4. The figure shows that the temperature coefficient of solubility increases with increasing magnesium content and shows that, at any given temperature, the uranium solubility decreases with increasing magnesium content.

Thermodynamic Studies in Metal Systems

At the May 1962 IAEA Symposium on Thermodynamics of Nuclear Materials, considerable information was reported on the thermodynamics of liquid-metal systems. The thermodynamics of the uranium-bismuth system were investigated by Rice, Balzhiser, and Ragone[50] in the temperature range of 1018 to 1115°K by measuring bismuth vapor pressures by an optical absorption technique and in the range of 873 to 1273°K by measuring the dissociation of UC_2 in bismuth. Wiswall and Egan[51] have reviewed all the published work on the thermochemistry of alloys of bismuth with thorium, protactinium, uranium, plutonium, and the high-yield fission products.

The thermodynamics of the binary systems of uranium with zinc, cadmium, gallium, indium, thallium, tin, and lead have been summarized by Johnson.[52] The various thermodynamic properties were determined largely by means of galvanic cells. Johnson related certain trends in the thermodynamic properties of the systems to the positions of the solute elements in the periodic table. Measurements of the zinc vapor pressure by dew-point determinations have been employed by Voigt at Ames Laboratory to obtain thermodynamic data for zinc-thorium, zinc-yttrium, and zinc-aluminum systems.[19]

Ackermann and Thorne[53] have reviewed the vaporization properties of uranium, plutonium, and thorium and their oxides. Vapor-pressure measurements in these metal systems are strongly affected by the presence of oxides. The free energies of uranium, thorium, and plutonium

were determined from reliable vapor-pressure measurements. The free energies of various oxide species were also determined.

Knowledge of phase diagrams and of the properties of the solid and liquid phases increases the utility of solubility data. Veleckis at Argonne has recently identified the phases in the neodymium-zinc system.[15] A report on the yttrium-zinc system, which was described in detail in the preceding Review,[54] has been issued.[55]

Construction Materials

Tungsten appears to be essentially inert to attack by molten zinc and for this reason has been selected as one of the construction materials for the skull recovery and blanket processes of the EBR-II fuel cycle. Zinc systems are employed as processing media in these processes. The high resistance of tungsten to corrosion by zinc has been corroborated by Chasanov[15] at Argonne, who was unable to detect any interaction of tungsten in zinc in powder compacts held at 650°C for 31 days.

Some stainless steels, which are severely attacked by molten zinc, suffer comparatively little attack by zinc vapor. Bennett at Argonne has recently determined the corrosion resistance of various stainless steels to zinc vapor.[15] In 500-hr exposures at 900°C, two austenitic 300-series stainless steels (types 304 and 347) underwent severe attack. Good corrosion resistance to attack by zinc vapor was exhibited by a 400-series stainless steel (type 405, a ferritic steel). Another 400-series stainless steel (type 440C) was less resistant to attack by zinc vapor than type 405 but nevertheless exhibited fairly good corrosion resistance.

Corrosion studies are under way at Brookhaven to evaluate the long-term corrosion resistance of materials, primarily carbon steels and refractory metals, to mercury and mercury vapor. The presence of zirconium or titanium at the cold point in boiling-mercury corrosion loops (operating between 600°F and about 1300°F) significantly reduces attack on carbon steels, $2\frac{1}{4}$ chromium–1 molybdenum steel, and Haynes 25 alloy.[1] The presence of zirconium in mercury also reduced corrosion in the condensing area, which is the location of the most severe attack in a boiling system. Attempts to determine the nature of the zirconium or titanium "protective films" by X-ray or electron-reflection diffraction techniques were unsuccessful.

A Mercury Corrosion Loop Testing Program is also under way at the Aerojet-General Corporation in California. Operation of the first of 10 loops has been started.[56] The corrosion and mass transfer resulting from the use of mercury as a thermodynamic working fluid are important considerations in the selection of materials for the SNAP-II system. The results of a study on corrosion and mass transfer in mercury and the corrosion mechanisms involved have been made available.[57]

Nikitin of Russia has summarized[58] the reaction of construction materials with various liquid metals (sodium and potassium and their alloys, lead, and bismuth) which have been proposed as reactor coolants. Diffusion mechanisms control corrosion in lead and bismuth systems; corrosion in sodium and potassium systems depends mostly on the amount of oxygen present. The corrosive effects of molten alkali metals on high-temperature materials have been reviewed by Amateau.[59] He indicates that the nitrogen content is also a very important factor in the corrosive effects of liquid metals, especially lithium.

Engineering Developments

Mixing and mass-transfer phenomena are being studied at BNL in fused-salt–liquid-metal extraction columns of the disk-and-doughnut type.[1] Cerium is being employed as the distributing solute between a NaCl-KCl-$MgCl_2$ eutectic and bismuth containing small concentrations of magnesium and zirconium. Preliminary mass-transfer results have been reported.

Other Nonaqueous Processes

Pyrochemical processing procedures, which are being applied principally to oxide and carbide reactor fuels, generally employ gases, molten salts, and liquid metals as reagents and reaction media. They are similar to pyrometallurgical processes in the use of high temperatures, a capability for handling short-cooled fuels, simplicity, and compactness. Since only moderate fission-product decontamination is achieved in both types of processes, the fuel

processing is usually integrated with remote fuel-fabrication procedures to form a complete fuel cycle.

Oxide Fuel Processing

At Hanford, development work has continued on the salt-cycle process, an electrolytic procedure for the recovery of irradiated uranium oxide–plutonium oxide fuel.[60–63] The mixed oxide fuel is dissolved in a molten-chloride salt bath by sparging the mixture with chlorine or hydrogen chloride. A portion of the resulting uranyl chloride in solution is reduced electrolytically at the cathode to uranium dioxide, which is essentially free of plutonium and is a by-product of the process. The plutonium and the remaining uranium are either codeposited as the dioxides in a second electrodeposition step or the plutonium is precipitated as plutonium dioxide by sparging the melt with a chlorine-oxygen mixture. This latter product is sufficiently enriched in plutonium so that it can be recycled to the reactor. The salt-cycle process is a part of the Plutonium Recycle Program, which is described in a recent progress report.[63]

As one aspect of fission-product release studies related to the processing of PRTR fuel, a few oxidation-rate measurements were made with uranium dioxide.[60] Bare sintered uranium dioxide cylinders $\frac{1}{2}$ in. in diameter and $\frac{3}{4}$ in. long were completely oxidized to U_3O_8 in $1\frac{1}{2}$ hr at 400 and 500°C. In 2 hr, 23% was oxidized at 300°C and 33% at 600°C. The relatively low oxidation rate at 600°C is attributed to the necessity for oxygen to diffuse through an adherent surface layer of U_3O_8 which is prevalent at about 600°C and above. The primary particle diameter of product obtained at 300 and 400°C was in the region of 2 to 4 μ.

"Vibration hammering" by means of an air hammer delivering 5000 blows per minute is being considered as a method of removing the vibrationally compacted PRTR fuel from the cladding. Hammering of a 1-ft-long section of Zircaloy-clad fuel rod irradiated to 1200 Mwd/ton by this technique resulted in successful removal of the uranium dioxide.

Reactions of Uranium Oxides in Molten-Chloride Media

Electromotive-force measurements have been reported previously[64,65] for the reaction

$$UO_2(s) + Cl_2(g) = UO_2Cl_2(\text{solution}) \quad (1)$$

in molten-chloride salts. Further measurements[60] have been made at several temperatures in sodium chloride–lithium chloride melts of various proportions in order to determine the effect of chloride-ion activity on the thermodynamics of the reaction. A typical S-shaped titration type curve was obtained when the electromotive force was plotted against the sodium chloride concentration in mole percent. The steep part of the curve appeared in the vicinity of the sodium chloride–lithium chloride eutectic (about 25 mole% sodium chloride). At 850°K the horizontal sections of the curve appeared at about 0.50 volt in melts containing less than 20 mole % sodium chloride and at about 0.52 to 0.53 volt in melts containing over 30 mole % sodium chloride, which is a region of higher chloride-ion activity. These results imply that two complex forms of uranyl chloride occur in this system.

It was reported previously[64] that impedance measurements had shown evidence of a U(V) species in molten-chloride media. More recently, spectrophotometric evidence of a U(V) species has been obtained both at Hanford[62] and at Argonne.[66] A characteristic spectrum with strong absorption peaks at 1530, 790, and 630 mμ was reported by workers at Hanford.[62] The U(V) species was obtained in concentrations estimated at 0.1 wt.% by (1) addition of uranium dioxide to a chloride melt containing about 10 wt.% U(VI) and (2) sparging a melt containing 10 wt.% U(VI) at 550°C with a hydrogen–hydrogen chloride mixture. The U(V) species is reduced to U(IV) by a rapid first-order reaction upon sparging with a hydrogen–hydrogen chloride mixture at 400°C, and it is oxidized rapidly by oxygen and chlorine. In the work at Argonne,[66,67] a similar spectrum was obtained upon the addition of the higher uranium oxides to lithium chloride–magnesium chloride melts. When uranium trioxide was added to this salt mixture, the following reaction was observed:

$$2UO_3(s) + MgCl_2(\text{solution}) = MgUO_4(s) + UO_2Cl_2(\text{solution}) \quad (2)$$

This reaction appeared to be followed by two subsequent reactions:

$$MgUO_4(s) + MgCl_2(\text{solution}) = UO_2Cl_2(\text{solution}) + 2MgO(s) \quad (3)$$

$$UO_2Cl_2(\text{solution}) \rightleftharpoons UO_2Cl(\text{solution}) + \tfrac{1}{2}Cl_2(g) \quad (4)$$

When the melt was exposed to air or chlorine, the spectrum attributed to U(V) disappeared rapidly and uranyl ion formed. The thermal decomposition of uranyl chloride (reaction 4) was investigated by adding uranyl chloride to equimolar lithium chloride–potassium chloride and to the sodium chloride–potassium chloride–magnesium chloride eutectic.[67] In each solvent the U(V) spectrum increased progressively with rising temperature from 500 to 800°C (see Fig. III-5). At constant temperature the spectra did not change further with time.

A further indication of the reversibility of reaction 4 was obtained by varying the chlorine pressure over the system.[67] As chlorine was removed from the system, a continual increase in the absorbance of the system was evident (Fig. III-6); when 500-mm chlorine pressure was added to the system, the absorbance decreased markedly. The family of curves in Fig. III-6 shows an isosbestic point at about 590 mμ, indicating only two absorbing species with a constant total concentration. The two species are very likely UO_2^{2+} and UO_2^{+} ions.

Carbide Fuel Processing

The development of three low-decontamination pyrochemical processes for the recovery of irradiated uranium carbide fuels has continued at Atomics International.[68–70] In one process the uranium carbide is oxidized at low temperatures (400 to 500°C); the resultant uranium oxide is then reconverted to the carbide by reaction with carbon at temperatures of 1300°C and above. The second process entails a conversion of the uranium carbide to a mixture of uranium nitride and carbon by reaction with nitrogen at about 900°C. Uranium monocarbide is regenerated from this mixture by heating it in vacuum at temperatures above 1500°C. In the third process the uranium carbide is electrolyzed in a molten-chloride bath, and dendritic uranium metal is deposited on a molybdenum cathode. The uranium deposit is dissolved in hot mercury and is converted to uranium monocarbide by distilling off the mercury in a propane atmosphere.

Significant fission-product removals have been effected during the carbothermic reduction of uranium dioxide to form uranium monocarbide.[69] Results of experiments employing uranium dioxide irradiated to about 10^{19} nvt and cooled five years are presented in Table III-1. Three carbon-to-uranium dioxide ratios were used in the starting materials. In one set of runs, the reaction conditions were 3 hr at temperatures of 1560, 1760, and 1940°C. In another set the reduction was carried out at 1900°C for 3 hr, and then the product was arc melted. The rare-earth fission products are expected to show the same behavior as cerium. Essentially no ruthenium was removed. The extent to which the carbide-forming elements (plutonium, cerium, and rare earths) are removed tends to decrease with increasing carbon content.

Because of the plutonium loss that occurs upon arc melting and the difficulties associated with remotely operated equipment, an effort is being made to develop other methods of fabrication.[70] In one approach, hypostoichiometric (carbon deficient) uranium monocarbide is prepared by heating U_3O_8 and carbon in a 1:6 mole ratio in a graphite crucible under vacuum. The product melts in the last stages of the reaction at 1700 to 1900°C. On cooling, this material forms fine grains of uranium monocarbide in a matrix of uranium metal. If this material is allowed to react with hydrogen at 200 to 220°C, it can be recovered from the crucible as a mixture of uranium hydride powder and small crystals of uranium mono-

Table III-1 PERCENT REMOVAL OF FISSION PRODUCTS AND PLUTONIUM DURING CARBOTHERMIC REDUCTION OF IRRADIATED URANIUM DIOXIDE[69]

Element	Starting ratio, C : UO_2*	Percent removal of element			
		Reduction temperature			Arc melted†
		1560°C	1760°C	1940°C	
Plutonium	3.17	6		17	80
	3.00	6		33	94
	2.88	14	38	46	98
Cerium	3.17	22		30	84
	3.00	14		44	97
	2.88	17	37	71	98
Strontium	3.17	98+		99+	99.9+
	3.00	98+		99+	99.9+
	2.88	97+	99+	99+	99.9+
Cesium	3.17	97+		99+	99+
	3.00	97+		99+	99+
	2.88	97+	98+	99+	99+

*Uranium dioxide irradiated to about 10^{19} nvt and cooled five years.

†Material prepared by reduction for 3 hr at 1900°C and then arc melted.

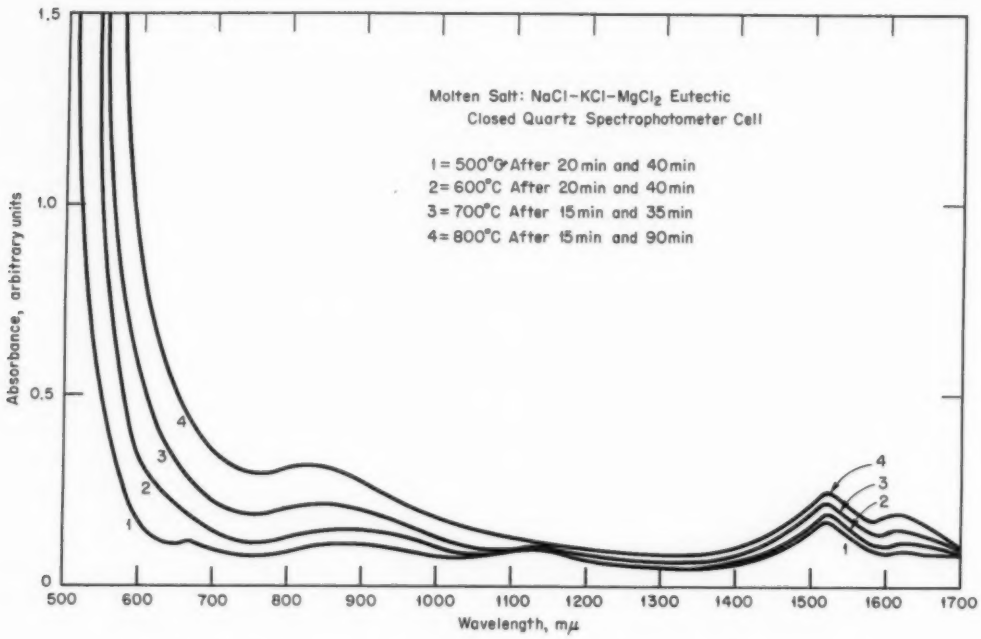
Molten Salt: NaCl-KCl-MgCl2 Eutectic
Closed Quartz Spectrophotometer Cell
1 = 500°C After 20 min and 40 min
2 = 600°C After 20 min and 40 min
3 = 700°C After 15 min and 35 min
4 = 800°C After 15 min and 90 min
Absorbance, arbitrary units
Wavelength, mμ

Fig. III-5 Effect of temperature on thermal decomposition of uranyl chloride.[67]

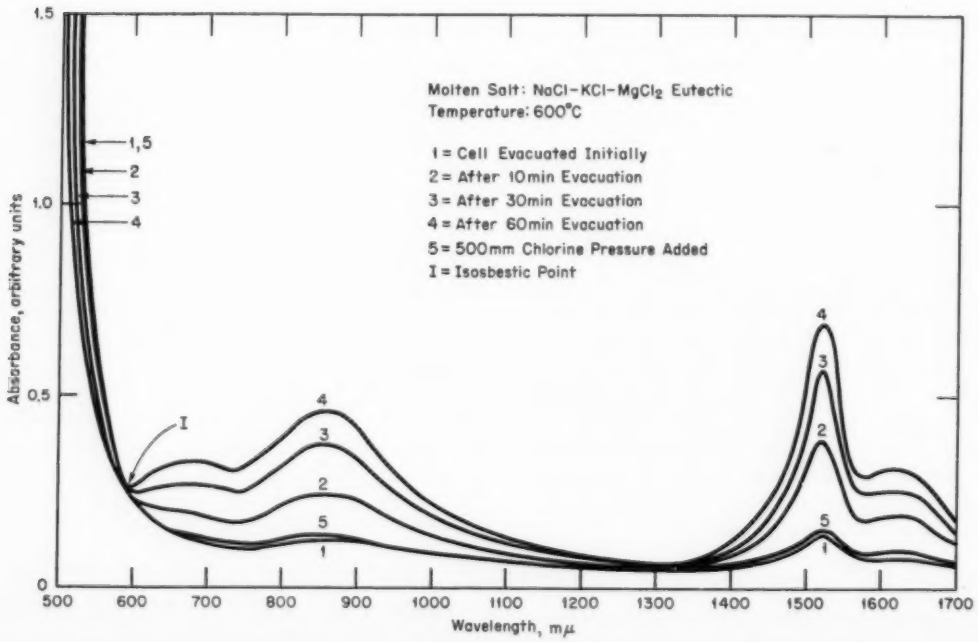
Molten Salt: NaCl-KCl-MgCl2 Eutectic
Temperature: 600°C
1 = Cell Evacuated Initially
2 = After 10 min Evacuation
3 = After 30 min Evacuation
4 = After 60 min Evacuation
5 = 500 mm Chlorine Pressure Added
I = Isosbestic Point
Absorbance, arbitrary units
Wavelength, mμ

Fig. III-6 Effect of chlorine removal on thermal decomposition of uranium chloride.[67]

carbide. Treatment of this mixture with a hydrocarbon should then produce a uranium carbide product which has a controllable uranium-to-carbon ratio and which can be pressed and sintered. In a second approach, uranium monocarbide suitable as a feed for vibratory compaction is prepared by the reaction of uranium oxide with excess carbon.

Table III-2 100-G TESTS EVALUATING THE CONVERSION OF U_3O_8 TO URANIUM MONOCARBIDE[69]

Charge ratio (gram atoms of carbon per mole of U_3O_8)	10.07	10.13	10.19
As-reacted UC product			
Carbon analysis, wt.%			
Average	4.77 ± 0.05	4.92 ± 0.08	4.95 ± 0.06
Median	4.75	4.87	4.95
Calculated carbon content, wt.%*	4.82	4.91	5.00
Air-firing weight gain, %	12.05 ± 0.07	11.97 ± 0.08	11.95 ± 0.02
Oxygen content, ppm†	2100	1300	1200
Arc-melted UC product			
Carbon analysis, wt.%	4.68 ± 0.02	4.74 ± 0.05	4.85 ± 0.03

*Assumptions are that 1.06 atoms of carbon are consumed in reducing U_3O_8 to $UO_{2.00}$ and that 3 gram atoms of carbon per mole of uranium dioxide are used in complete conversion to uranium monocarbide.

†Values are based on carbon analyses and weight-gain data. Most of this oxygen content is attributed to hydrolysis after removal of the product from the furnace.

Scale-up of the carbothermic reduction reaction is being investigated, a primary objective being to obtain a consistent, controllable carbon content of the product. Preliminary thermobalance experiments showed that 1.0 to 1.1 moles of carbon were consistently required to reduce 1 mole of U_3O_8 to uranium dioxide.[69] It therefore appears that uranium monocarbide of controlled carbon content can be prepared directly from U_3O_8 powder. This method has the advantages of (1) starting with a stable material having a fixed oxygen content, (2) eliminating the hydrogen-reduction step used when the carbide is processed by the oxidation method, and (3) less agglomeration of the oxide used in the carbothermic reduction. In small-scale tests the carbon reduction of U_3O_8 to $UO_{2.00}$ required about $2\frac{1}{2}$ hr in vacuum at temperatures up to 1100°C. Further reduction to the monocarbide was complete after $4\frac{1}{2}$ additional hours at 1700°C in vacuum. The as-reacted product had a carbon content of 4.80 ± 0.02 wt.% (the theoretical value for uranium monocarbide is 4.80).

When the procedure was scaled up to 100-g batches of U_3O_8, the oxide was reduced to uranium dioxide after $3\frac{1}{2}$ hr in vacuum at temperatures up to 1100°C, and the formation of uranium monocarbide was complete after seven additional hours at increasing temperatures up to 1700°C. Analytical data on the product, both as-reacted and after arc melting, are given[69] in Table III-2. The results agree with the thermobalance data, i.e., about 1.06 gram atoms of carbon were required to reduce 1 mole of U_3O_8, and the empirically determined carbon-to-U_3O_8 starting ratio of 10.06 produced very nearly stoichiometric uranium monocarbide. Carbon analyses of the arc-melted samples indicate that the oxygen content in the products at the time of arc melting probably did not exceed about 1000 ppm.

In view of the consistent results obtained with U_3O_8 from different sources and the reproducibility of the reduction reactions, U_3O_8 appears to be a suitable starting material for the production of uranium monocarbide.[69]

In the second process under study at Atomics International, the uranium carbide nitridation process, kinetic measurements have shown that reconversion of the nitride to carbide proceeds by a two-step reaction.[70] The first reaction is zero order, with an activation energy of 91 ± 12 kcal/mole. The second reaction follows a parabolic rate law, with an activation energy of 31.3 ± 1.1 kcal/mole.

Some work on the electrolytic process (the third process being studied by Atomics International) has been reported in which cathode materials other than molybdenum were used. A rotating stainless-steel cathode gave a good

uranium deposit from a lithium chloride–potassium chloride–uranium tetrafluoride melt. Cathode efficiencies were 32, 16, and 37% in three runs.[69] A liquid cadmium cathode produced good efficiencies when it was used with a uranium anode, but not when it was used with a uranium carbide anode, in a lithium chloride–potassium chloride–U(III) chloride melt:[70]

Anode	Cathode efficiency, %	Anode efficiency, %
U	73.1	100.2
UC	3.2	35.6
U	77.5	97.8

To investigate this behavior further, the potentials of the following cells were measured[70] at 450°C:

$U\|LiCl, KCl, UCl_3\|\|LiCl, KCl, AgCl\|Ag$	1.390 ± 0.020 volts
$UC\|LiCl, KCl, UCl_3\|\|LiCl, KCl, AgCl\|Ag$	0.700 ± 0.050 volt

The U(III) chloride and silver chloride concentrations were 12.5 wt.% and 1.06 mole %, respectively.

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Section

IV

Reactor Fuel Processing

Waste Disposal

Treatment of Liquid Wastes by Ion Exchange and Foam Separation

Ion Exchange

Laboratory-scale studies of the reactions of Cs^{137} and Sr^{90} with ion-exchange minerals are being made at Oak Ridge National Laboratory (ORNL).[1–4] Vermiculite was used in the studies with Cs^{137}, whereas rock phosphate and gibbsite (aluminum hydroxide) were used in the studies with Sr^{90}.

The use of vermiculite systems for the removal of cesium is of interest for two reasons: (1) vermiculite is one of the few clay minerals with a sufficiently large particle size to be of practical use in waste decontamination by ion-exchange columns, and (2) when vermiculite is treated with one of the heavier alkali-metal cations or ammonia, the lattice spacing changes measurably and results in steric effects that have improved the exchange properties of vermiculite for cesium.

Pretreatment of the vermiculite with potassium leads to the collapse of the vermiculite lattice and thereby increases the number of exchange sites at the edges of collapsed basal spacings, where cesium can be incorporated into the lattice by "edge fixation."[2,4] This increased the distribution coefficient (K_d) for cesium between 0.5M sodium nitrate and the treated vermiculite by a factor of 2.7.

In another ORNL investigation, influent feed streams containing added potassium of varying concentrations were passed through untreated vermiculite columns. The addition of the potassium to the influent stream also caused the lattice to collapse. However, in these runs the cesium was entrapped by "interlayer fixation." A drop in the exchange capacity of the vermiculite and a decrease in the percentage of cesium leached was noted as the potassium concentration in the influent stream was increased. Although the potassium is competitive with cesium for the interlayer fixation sites, the K_d for cesium between 0.5M sodium nitrate and the vermiculite increases with increasing potassium concentration, passing through a maximum K_d of 727 at 0.04M potassium nitrate.

The percentage of the cesium leached is more directly related to the exchange capacity than to the cesium K_d and decreases with decreasing exchange capacity. This is due to a shift from edge fixation to interlayer fixation as the dominant sorption mechanism. As a greater fraction of the cesium occupies interlayer fixation sites, it is less readily leached.

The addition of other heavy alkali-metal cations (cesium and rubidium) and ammonium ions to the influent feed stream also causes collapse of the vermiculite lattice. Since they are more strongly held than potassium, a smaller concentration of the heavy alkali-metal cations and ammonium ions are required in 0.5M sodium nitrate to initiate lattice collapse and to obtain optimum cesium removals. The K_d of the ammonium-treated influent was higher, but the percentage of cesium leached was also much greater than for the alkali-metal cations.

The effect of temperature on exchange reactions was investigated.[4] As expected, increased temperatures resulted in faster rates of the exchange reactions, but the effect on cesium sorption is influenced by other exchange reactions occurring in the system. When 0.5M $NaNO_3$ containing added Cs^{137} was passed through columns of sodium- or potassium-treated ver-

miculite, a more rapid release of potassium from the collapsed layers was favored at higher temperatures (81°C) and resulted in a greater degree of lattice expansion. This resulted in a higher exchange capacity and a lower cesium K_d.

ORNL also investigated the use of rock phosphate for the removal of Sr^{90} from waste solutions.[1,4] Rock phosphate contains the mineral apatite $[CaFCa_4(PO_4)_3]$ which, when used in basic media, is highly selective in the removal of strontium. Calcite (calcium carbonate) has also been reported[1] to be effective in the removal of strontium. Calcite columns have high efficiency for removing strontium when the influent solution to the column is basic and contains added phosphate ion. The removal of strontium by a column of calcite was tested by passage of a simulated waste solution containing 0.05M $NaNO_3$, 0.006M NaOH, 0.01 ppm Sr^{2+}, trace amounts of Sr^{85}, and 120 ppm PO_4^{3-}. The calcite column exhibited a maximum decontamination factor (influent activity/effluent activity) of 100 after 600 bed volumes. The saturation capacity of 20.0 g of calcite was of the order of 10,000 bed volumes.

The effects of sodium-ion concentration and of phosphate additions on strontium removal were tested in five laboratory columns containing rock phosphate. In these tests a simulated waste solution (columns 1, 2, and 3) and an ORNL plant waste solution that had been clarified and filtered (columns 4 and 5) were used. Strontium-85 was added to the simulated waste solution as the tracer activity in columns 1 to 3.

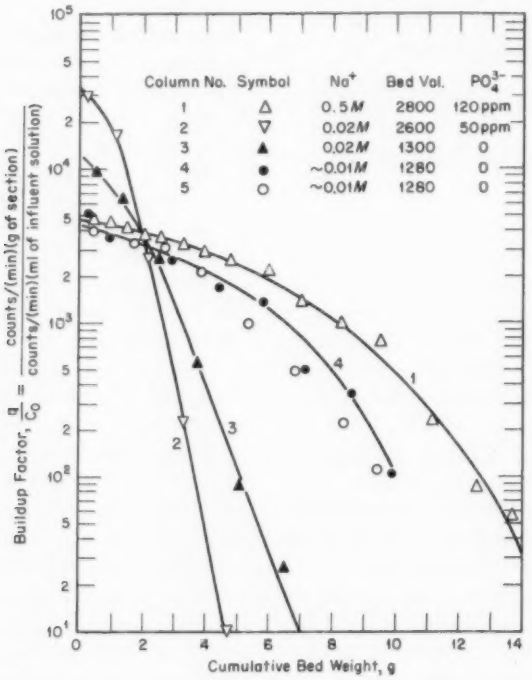
Column No. Symbol Na+ Bed Vol. PO4 3-
1 0.5M 2800 120 ppm
2 0.02M 2600 50 ppm
3 0.02M 1300 0
4 ~0.01M 1280 0
5 ~0.01M 1280 0
Buildup Factor, q/C0 = counts/(min)(g of section) / counts/(min)(ml of influent solution)
Cumulative Bed Weight, g

Fig. IV-1 Strontium removal by rock phosphate columns.[4]

The results of these column tests are shown in Fig. IV-1. The abscissa is plotted as cumulative bed weight, which is directly proportional to bed depth. The ordinate is plotted as "buildup" factor, q/C_0, where q is the average activity per gram of column section and C_0 is the average activity per milliliter of influent solution. A comparison of the results from the tests in columns 1 and 2 showed that high (0.5M) sodium-ion concentration was definitely detrimental for the rock phosphate column; a buildup factor of 3×10^4 was determined after about

2600 bed volumes. The Sr^{85} activity in test column 2 did not move down as far as the activity observed in test column 1. Thus, unlike the calcite column, high sodium concentration is detrimental for optimum performance for the rock phosphate column.

Column 2 was used to test the effect of adding small amounts of phosphate to the test solution. The curve in Fig. IV-1 shows that, in column 2, which contained 50 ppm phosphate, the strontium activity traveled a shorter distance down the column after passage of about 2600 bed volumes of simulated waste than the distance traveled by the activity in column 3 after passage of 1300 bed volumes of waste that did not contain phosphate. A possible explanation for the role of phosphate in this rock phosphate system is the mineral content of the rock phosphate ore. If the material contained calcite, then the phosphate may be necessary to prevent the calcite from interfering, as well as to aid strontium removal by acting as a sorbent through the calcite-phosphate reaction.

In test column 4, ORNL laboratory waste solution was used. The *p*H of the solution was about 12, and the calcium content was 1×10^{-4} meq/ml. The sodium concentration was not known but was probably of the order of 0.01 *M*. Operating conditions in the test with column 4 were the same as those used in the test with column 3. The decontamination factor obtained with column 4 was of the order of 1000. The activity traveled farther down in column 4 than in column 3 after passage of about 1300 bed volumes in each column. The buildup factor for column 4 was approximately 5000; the reduction in buildup was attributed to the approximately 400-fold increase in the calcium-strontium concentration of the waste solution.

In test column 5, the ORNL plant waste solution was treated with ethylenediaminetetraacetic acid (EDTA) in order to reduce the calcium-ion concentration from 1×10^{-4} to 5×10^{-6} meq/ml. The data show that, at this concentration level, EDTA did not have a strong detrimental effect on strontium removal by the rock phosphate. This observation may be significant since complexing agents are known to affect the efficiencies of removal of strontium in actual waste solutions.

Table IV-1 COMPARISON OF AN ION-EXCHANGE RESIN, CALCITE, AND ROCK PHOSPHATE FOR Sr^{90} REMOVAL FROM WASTE[4]

Ion-exchange material	*p*H required	Phosphate required	Buildup factor*	Decontamination factor	Cost	Effect of calcium ion in the waste
Resin†	12	None	1,000	1,000	$50 per cubic foot	Slightly detrimental
Calcite	11 to 12	50 to 100 ppm	10,000	100	Mostly transportation	Highly detrimental
Rock phosphate	10	None	5,000	1,000	Mostly transportation	Slightly detrimental

*Buildup factor $= \frac{q}{C_0} = \frac{\text{average activity per gram of column section}}{\text{average activity per milliliter of influent solution}}$.

†Phenolic-carboxylic cation-exchange resin Duolite CS-100. The operating conditions of the column in this test were similar to that used in rock phosphate study.

In Table IV-1 the removals of Sr^{90} from waste solution are compared for various ion-exchange materials (a cation-exchange resin, calcite, and rock phosphate). The cation-exchange resin data were obtained for columns which had the same diameter as in the calcite and rock phosphate tests but which contained 25 cm of resin rather than 10 g of calcite or rock phosphate. Calcite requires 50 to 100 ppm phosphate ions in addition to the high *p*H. Both calcite and rock phosphate are relatively cheap materials compared with the resin (Duolite CS-100); calcite does show a high buildup factor. However, if one reduces the concentration of sodium ion, which is not required for the rock phosphate column, buildup factors greater than 10,000 can also be obtained for rock phosphate.

A highly selective sorbent for strontium has been prepared by heating gibbsite [$Al(OH)_3$] above its decomposition temperature[3-5] of 150°C. The heating resulted in the formation of aluminum oxides with high surface area (greater than 200 m^2/g), in contrast to the low surface area (about 0.3 m^2/g) for gibbsite. Distribution coefficients (K_d) for Sr^{90} ranged from 4000 to 40,000 when the solid-to-solution ratio was increased from 0.001 to 0.05 g/50 ml. A raw aluminum ore (bauxite from Arkansas)

containing 40% gibbsite also exhibited good strontium-sorbing properties when the gibbsite component was decomposed by heating.

At Hanford two ion-exchange runs were made in the Micro Pilot Plant (MPP) to investigate the ion-exchange removal of ruthenium from Purex tank-farm condensate and to gain a better understanding of the ruthenium removal mechanism.[6,7] In the first run, only about 20% of the ruthenium was removed from a Purex tank-farm condensate that was steam stripped, acidified to a *p*H of 4.2, and passed through a bed of Amberlite IR-120 (the sodium form). This 20% removal of ruthenium may be compared with the more than 95% removal of ruthenium from a steam-stripped acidified Purex tank-farm condensate feed that was passed through a bed of activated carbon prior to being passed through a bed of Amberlite IR-120 (the sodium form). In the second run a feed solution that was similar in composition to the feed solution in the first run was passed through a bed of Illco NR-2 (a strongly basic anion-exchange resin in the hydroxyl form). The removal of ruthenium decreased from 85% at the beginning of the run to about 70% at the end of the run.

The results of these two runs appear to indicate that the ruthenium is present primarily in the anionic form but that some of it is present in the cationic form. Although combined treatments of cation and anion exchange efficiently remove ruthenium, the presence of nitrates and nitrites in the condensate waste reduces the efficiency.

Studies of the reactions of Cs^{137} and Sr^{90} with mineral ion exchangers have been described in two papers[8,9] by Ames at Hanford. In the first paper[8] Ames summarized the results of an investigation of the kinetics of cesium exchange for sodium in the film diffusion region for several mineral ion exchangers. The cesium diffusion-film thickness was computed by two methods with comparable results. The determination of fundamental kinetic quantities, such as particle diffusion coefficients and average film depths, allows computation and prediction of loads and loading rates of the mineral exchange materials for given experimental conditions. In the second paper[9] Ames has shown how equilibrium, statistical, and kinetic data can be used for the selection of a zeolite for the specific removal of a cation under given conditions. In this study several zeolites were examined for their ability to remove strontium from wastes containing high concentrations of sodium.

Mathers and Watson[10] at Chalk River have described the disposal by ion-exchange treatment of 8200 liters of acid waste with clinoptilolite. The waste solution was of intermediate activity and contained 400 curies of cesium, 370 curies of Sr^{90}, about 0.2 curie of plutonium, and about 0.4 curie of americium. (The disposal of 18,000 gal of a moderately radioactive acid-waste solution by conversion to a cement mortar was described in a previous issue of *Reactor Fuel Processing*.[11]) This waste solution, which was 10 years old, was composed of various solutions (nitric, oxalic, and tartaric acids and sodium hydroxide) that had been used for the decontamination of equipment. The clinoptilolite (which was pretreated with nitric acid) was contained in an open-top reinforced-concrete vessel whose inside walls were asphalt coated. The acid-waste solution was neutralized with sodium hydroxide and diluted with water to a *p*H of 2.8 before being fed to the clinoptilolite column. The run resulted in the satisfactory removal of the radioactive elements from the waste solution, and at the end of the run a concrete cover was poured on top of the mineral column and the seam between the cover and vessel was sealed with asphalt. The concrete container was then buried in sand at the Chalk River disposal area.

Foam Separation

ORNL is continuing its investigation of the removal of Sr^{90} from ORNL low-activity wastes using a foam-separation process.[3,12] Previously reported studies[13] with ORNL tap water have shown that the removal of strontium from low-activity-level wastes by foam separation is greatly facilitated if the waste is pretreated to reduce the concentrations of dissolved calcium and magnesium to 1 to 2 ppm (as calcium). This pretreatment process consisted of precipitation of the magnesium and calcium by the addition of 5×10^{-3} *M* each of sodium hydroxide and sodium carbonate, coagulation with 1 or 2 ppm ferric ion, and the clarification in a gently agitated sludge-column clarifier (see Fig. IV-2). In a 100-hr continuous run[3] with ORNL low-activity waste, this process decreased the average hardness to 1.9 ppm (as calcium). The average decontamination factor for strontium during the run was 10. This may be compared

with a decontamination factor for strontium of about 100 when using ORNL tap water.[12] The overall decontamination factor for strontium was increased to about 20 by passing the softened effluent from the clarifier through an agitated bed of calcium carbonate. The treatment also further reduced the calcium and magnesium hardness from about 2 to 1 ppm (as calcium).

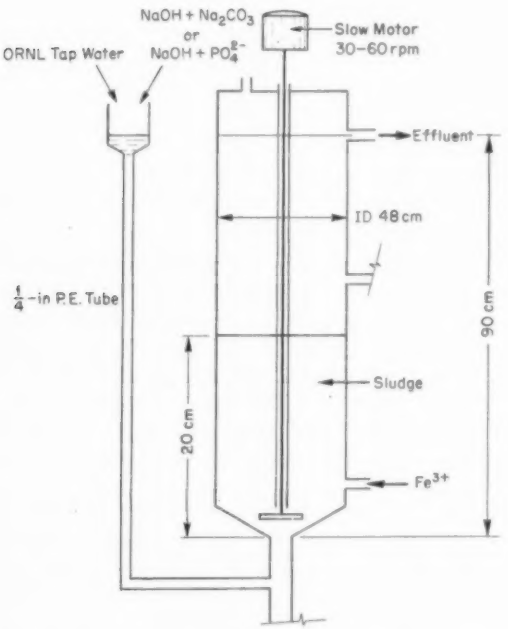

Fig. IV-2 Laboratory-scale sludge-column clarifier used in one-step process pretreatment tests.[12]

Materials in ORNL low-activity waste which might interfere with precipitation of calcium and magnesium by treatment with either NaOH or Na_2CO_3-NaOH are Turco 4234, Fab, and components of these proprietary formulations, such as sodium dodecylbenzene sulfonate, sodium hexametaphosphate, sodium tripolyphosphate, and sodium pyrophosphate.[3,12] In beaker tests with ORNL tap water and ORNL low-level-activity plant waste solution, the effect of these impurities on the reduction of calcium and magnesium hardness was determined. The ORNL tap water and ORNL low-level-activity plant waste solution each contained about 65 ppm calcium and about 35 ppm magnesium (both calculated as calcium carbonate). With ORNL tap water made 0.01 *M* in sodium hydroxide, the addition of Turco 4234, Fab, sodium hexametaphosphate, sodium pyrophosphate, and sodium orthophosphate, each at concentrations of 1.5 to 3 ppm, inhibited the precipitation of calcium. This interference is reduced when the tap water is made 0.005 *M* in Na_2CO_3–0.01 *M* in NaOH and is nearly eliminated in 0.005 *M* Na_2CO_3–0.005 *M* NaOH.

Since beaker tests of ORNL tap water indicated that the precipitation of calcium orthophosphate is not inhibited by the presence of other phosphates, such as hexametaphosphate, a continuous run[12] with the ORNL low-level-activity waste solution was performed in the laboratory-scale clarifier in which the waste was made 0.004 *M* in NaOH and 50 ppm in phosphate, as trisodium phosphate. The *p*H of the resulting solution was 11.2. The calcium in the clarifier effluent stream was reduced to 2.5 ppm (as calcium), and a decontamination factor for strontium of 15 to 20 was achieved. Passing the effluent from the clarifier through a stirred bed of calcium carbonate reduced the calcium hardness further to 1.2 ppm.

Conversion of High-Level-Activity Wastes to Solids

Spray Calcination

Hanford has completed the installation of radiant-heat spray-calcination and pot-calcination processing equipment in the High-Level Radiochemistry Facility.[7,14]

In radiant-heat spray calcination, the solution is atomized at the top of a heated spray column that is maintained at 700 to 750°C. Complete drying of the spray droplets and some salt decomposition are achieved by radiant energy from the spray column. The dried residue falls into a melt pot. Further decomposition and melting of the dried residue take place continuously in the melt pot that is maintained well above the melting temperature of the dried residue, typically 750°C. The entire operation is continuous, within the limits of the capacity of the melt pot. The off-gas is more nearly uniform in both flow and composition (an advantage over pot calcination) and hence more easily handled by the off-gas decontamination equipment. Also, there is much less spatter-

ing and crusting in the pot, resulting in a "cleaner" melt and a greater effective capacity of the pot.

In pot calcination the solution is fed directly into a cylindrical pot that is inductively heated. By adjustment of the feed rate and of the heat input, the pot is maintained about one-half full and is therefore operating as a semicontinuous concentrator. On completion of the feed cycle (typically 4 to 8 pot volumes), heating is continued to dryness. The heat input is then increased to bring the temperature of the waste to about 800°C. The waste is held at 800°C for about 1 hr to bring about denitration, desulfation, and melting. The pot is then allowed to cool.

The radiant-heat spray calciner and melt-pot calciner were operationally tested with Purex 1WW feeds containing added tracer-level activity and with full plant-level-activity Purex 1WW feed. The two calciner units performed satisfactorily, yielding a dry, melted product. Operation with full plant-level-activity feed was very smooth and uneventful. The use of full plant-level-activity Purex 1WW represents the first time that an actual fuel-processing plant high-level-activity waste has been calcined on a pilot-plant scale. At the time of calcination, the waste was about 200 days old (from reactor discharge); hence I^{131} was virtually absent. A volume reduction factor equivalent to about 13 for actual Purex-plant 1WW waste was achieved. This corresponds to about 0.5 cu ft of solid melt (at 2.5 to 3 g/cm^3) for the waste from 1 ton of uranium. In the spray-calcination runs, the waste from about 0.25 ton of uranium was contained in one 4-liter pot. The centerline temperature in this 5-in.-diameter pot was maintained at a little over 100°C by the radioactivity present in the 200-day-old waste. There has been no discernible pressure buildup in the sealed pots.

Data from a radiant-heat spray-calcination run, using actual plant Purex 1WW, indicated that less than 0.1% of the fission products other than ruthenium reached the off-gas condenser. Ruthenium found in the condensate averaged about 15% of the original amount present in the feed, but the ruthenium decontamination factor for the condenser was over 10^4. About 88% of the ruthenium passing the condenser was removed by the scrubbers, 8% by the silica gel, and 4% by the Cambridge "absolute" filters, giving an overall ruthenium decontamination factor in excess of 10^9 (analytical detection limit). No activity other than ruthenium was detected beyond the scrubbers.

Fluid-Bed Calcination

At the ICPP a fluidized-bed calcination process for high-level-activity aluminum nitrate wastes continues to be investigated.[15–24] Pilot-plant studies of this process with nonradioactive material are currently being conducted in a 12-in.-diameter electrically heated unit and a 24-in.-square NaK-heated unit. The 48-in.-diameter Demonstrational Waste Calcining Facility (DWCF) has been built for demonstration of this process with high-level-activity wastes. Testing of the DWCF with nonradioactive feeds is under way. A process equipment flow sheet for the demonstrational calcination unit is shown in Fig. IV-3.

The results of runs in the DWCF have shown that it could be continuously operated in a routine manner and that the solids which escape past the calciner primary cyclone to the liquid scrubbing system could be maintained at a satisfactory level.[16] The data indicate that the system is operable with a bed of either predominantly alpha alumina or predominantly amorphous alumina, but the acid solubility of the amorphous form and its greater resistance to attrition make it preferable from the standpoints of quantity of fine solids generated and of trouble-free handling of the scrubber solution and ease of decontamination.

Additional pilot-plant calciner runs[16] were made to investigate how the elutriation rate of solids from a fluidized bed is affected by the nozzle air rate and by the return of fines to the calciner bed. Three runs (29 to 31) were made in the 24-in.-square calciner. In these runs the crystalline structure of the alumina product was controlled either by adding boric acid to or by increasing the sodium nitrate content of the feed to the calciner. Alpha alumina was produced in runs 29 and 30 with a sodium nitrate concentration in the feed of 0.2*M*. No alpha alumina was detected in the bed material in run 31 when the boric acid concentration in the feed was 0.01*M*. The data from these runs also indicated that decreasing the nozzle air rate lowered both the calciner and solids elutriation rate and the solids carryover from the primary cyclone while introducing feed at a rate of 150 liters/hr to a bed

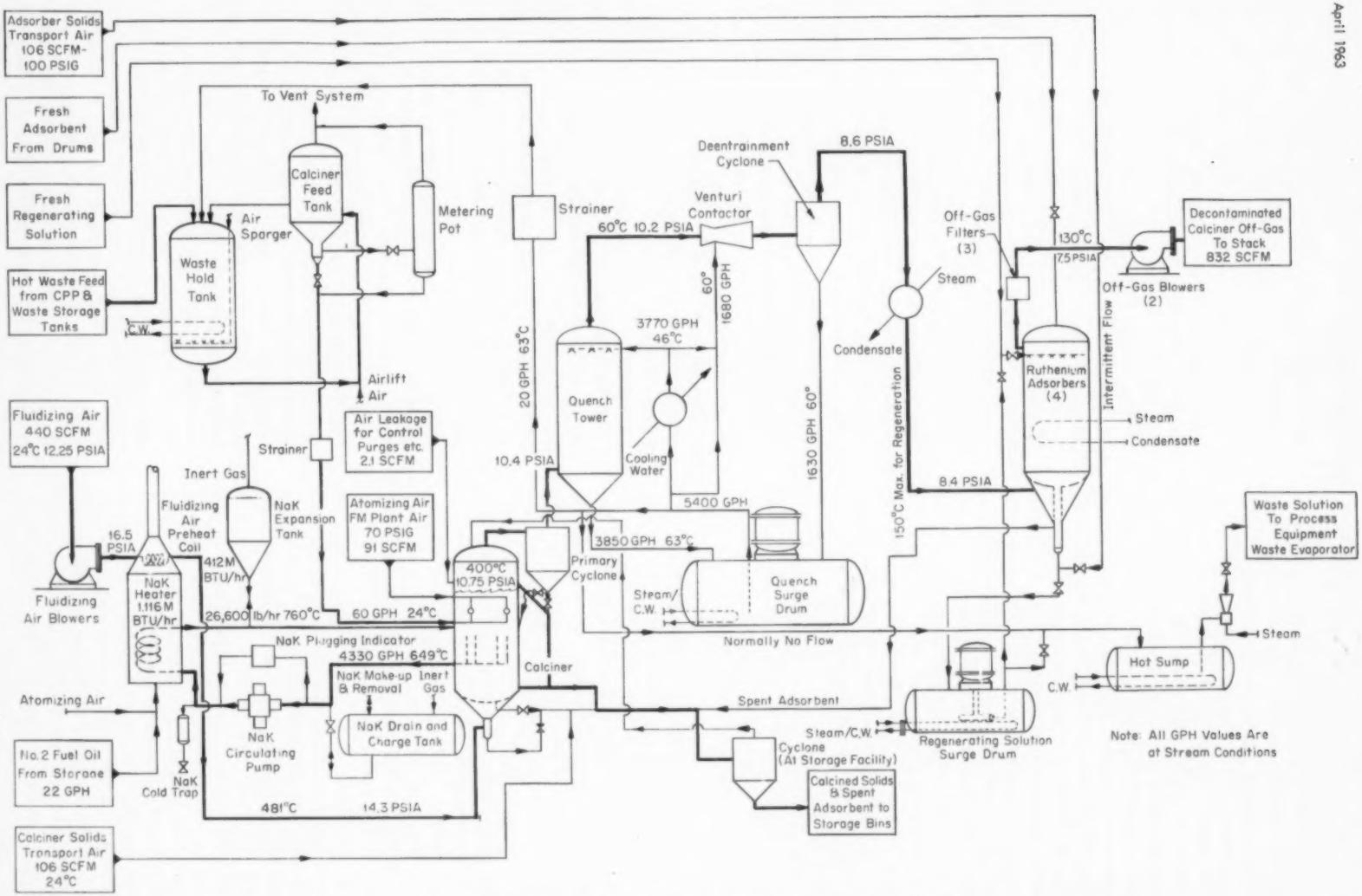

Fig. IV-3 Demonstrational-calcination-unit process flow sheet.[22]

containing 25 to 50% alpha alumina. The decreased nozzle air rate also resulted in a lowering of the alpha-alumina content of the solids elutriated from the calciner; at nozzle air-to-liquid volume ratio (NAR) of 150, only a trace of alpha alumina was found in the elutriated solids, whereas these solids generally contained about one-half of the alpha content of the bed. The elutriation rate of solids from the calciner increased markedly when the solids were returned to the bed. In run 30 with an alpha-alumina bed, the return of fines to the bed increased the elutriation rate from the calciner to a maximum of 24 kg/hr, which was about six times the elutriation rate obtained without fines return. In run 31, in which an amorphous bed was used, the return of fines to the bed increased the elutriation rate from the calciner to about 7 kg/hr, or about four times the elutriation rate obtained without fines return. The return of fines to the bed also resulted in higher concentrations of solids in the off-gas downstream of the calciner cyclone with both high- and low-alpha-alumina beds. High-alpha beds showed the highest carryover rates.

Seeding a bed with inert material for effective control of particle growth rate is desirable because high nozzle air flow rates for seed production also generate excessive fines that increase the solids loading of the calciner off-gas. Sand, which was introduced as seed particles to an amorphous bed in run 31, successfully controlled the particle growth rate of the bed at a lower NAR value (250) than was found necessary in the DWCF with the same nozzle size at the same conditions. The feed rate to the pilot-plant calciner was 150 liters/hr. On the basis of data from this run, the mass median particle diameter (particle size) of the calcined solids may be maintained at about 0.5 mm by using sand seed particles less than 0.1 mm in diameter and at a sand-addition flow rate of 2% of the calcined-solid-product rate.

The effect of boric acid and phosphoric acid[16] on aluminum nitrate calcination was investigated for the Idaho Chemical Processing Plant (ICPP) at the Stanford Research Institute. In laboratory calcination tests, in which either boric acid or phosphoric acid was added to the liquid feed, up to 4% alpha alumina was detected in the calcine of samples employing only 0.01*M* boric acid or 0.01*M* phosphoric acid, but alpha alumina was not detected in samples employing higher additive concentrations. A control sample without additives produced 36% alpha alumina. These results indicate that boric acid and phosphoric acid are equally effective in retarding the formation of alpha alumina.

The ICPP has issued several topical reports[17–22] that summarize its investigations on the development of a fluidized-bed calcination process for aluminum nitrate type wastes. These reports describe work performed in the laboratory and in the 24-in.-square NaK-heated pilot-plant calciner. Brown, Grimmett, and Buckham[17] have described the development of the 24-in.-square NaK-heated pilot-plant calciner and summarized the initial process results obtained in the operation of this calciner unit. The results of the first 10 extended runs made in this calciner unit are presented. Wheeler, Grimmett, and Buckham[18] have reported on the studies made in the 24-in.-square NaK-heated calciner to determine the effect of operating variables on the particle porosity of calcined alumina.

Murray and Rhodes[19,20] have described the laboratory investigation of the variables that affect the conversion of amorphous calcined alumina to crystalline alumina in the temperature range 350 to 650°C. Kelley[21] has presented the results of experimentally determined values for the thermal conductivity of alumina which was produced in the pilot-plant calciner. The measured thermal conductivity varied from 0.08 to 0.30 Btu/(hr)(sq ft)(°F/ft) at 100 and 2800°F, respectively. Above a temperature of 1800°F, the alumina converts from amorphous to alpha crystalline structure, and the curve of thermal conductivity vs. temperature is discontinuous in the region of 1800°F (see Fig. IV-4).

The thermal conductivity of +28 and −100 Tyler mesh fractions of calcined alumina in the temperature range 100 to 1000°F is shown in Fig. IV-5. It is significant to note that the thermal conductivity of the +28-mesh fraction increases rapidly with temperature, whereas the increase with the −100-mesh fraction is less rapid. This is probably due to the effect of particle size on the radiant heat transfer. This mechanism of heat transfer becomes a more significant part of the equivalent conductivity as temperature increases because, as the experimental results showed, with in-

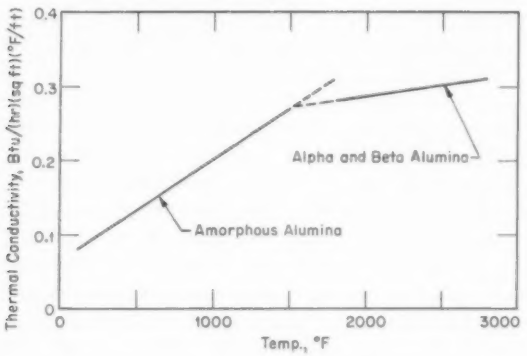

Fig. IV-4 Thermal conductivity of amorphous and crystalline forms of calcined alumina.[21]

creasing particle size, there were larger void spaces within the mass of solids.

Stevens[22] at ICPP has prepared an economic evaluation of fluid-bed calcining of the acidic and reacidified* forms of Purex and Thorex wastes. He has assumed that the fluidized-bed plant would convert to solids the radioactive wastes from a 6 metric ton/day nuclear fuel plant processing 1500 metric tons of uranium converter fuel per year at a burnup of 10,000 Mwd/metric ton and 270 metric tons of thorium converter fuel per year at a burnup of 20,000 Mwd/metric ton. This hypothetical nuclear fuel-processing plant is capable of processing all the fuel from a 15,000-Mw(e) nuclear economy. These are the same assumptions used by ORNL in its comprehensive study that was undertaken to evaluate the economics and hazards associated with alternative methods for ultimate disposal of highly radioactive liquid and solid wastes (see previous issues of *Reactor Fuel Processing*[15,23,24]).

The cost of fluid-bed calcining was determined at processing rates of 45, 60, and 75 gal/hr for storage of calcined solids in bins varying from 3 to 22 in. thick and installed in underground concrete vaults containing 4, 12, 20, and 40 nested annular bins, each nest with an overall diameter of up to 12.5 ft (see Fig. IV-6). The bins are vented, convection air cooled, and constructed of stainless-steel type 410. The thickness of the bin is dependent on the age, volume reduction factor, and thermal conductivity of the solids within the arbitrarily selected bin surface temperature of 300°F and centerline temperature of 1650°F.

The lowest cost, 0.47×10^{-2} mill/kw(e)-hr, was for processing acidic Purex and Thorex wastes at 75 gal/hr with storage in an underground concrete vault containing 40 of the 12.5-ft-diameter nested bin arrays. The highest cost, 2.9×10^{-2} mill/kw(e)-hr, was for processing reacidified Purex and Thorex wastes at 45 gal/hr with storage in an underground concrete vault containing four nested bin arrays.

*Reacidified wastes are acid wastes that have been neutralized for interim liquid-storage purposes. The neutralized wastes are then reacidified to avoid, during calcination, the formation of solid sodium nitrate that is not sufficiently stable in the presence of high temperatures and radiation for ultimate storage.

Pot Calcination

ORNL is continuing its investigation of the permanent disposal of high-level-activity liquid wastes by conversion of these liquid wastes to solids by high-temperature pot calcination or fixation in the final storage container (calciner pot) itself.[25] The calciner pots containing the calcined solids would be stored in a permanently dry environment such as a salt mine. Within present technology, the pot-calcination method appears to offer complete control of radioactivity during treatment, shipping, and storage. Design information is being developed for the construction of a pilot plant to be located at Hanford. Development work has been with synthetic Purex, Darex, and TBP-25 wastes containing no added fission-product activity. One phase of the ORNL program is concerned with

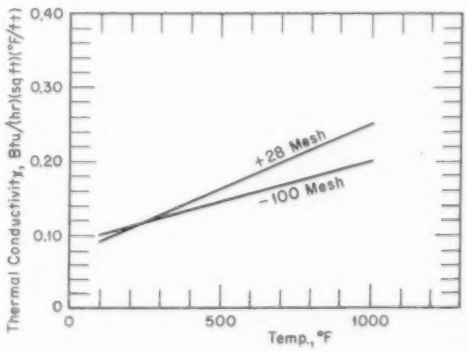

Fig. IV-5 Thermal conductivity of +28- and −100-mesh calcined alumina.[21]

direct calcination processes in which melting does not occur and little or no additives are combined with the wastes. In the second phase enough additives are to be used to induce melting to form a glasslike material in which the fission products are fixed.

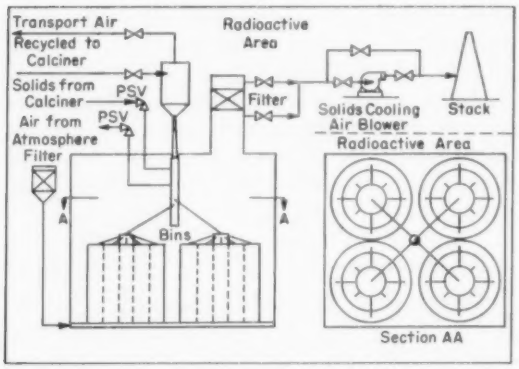

Fig. IV-6 Schematic diagram of bins for calcined solids storage and flow sheet for air cooling of bins.[22]

In two engineering-scale tests[3] simulated TBP-25 high-level-activity waste solutions were satisfactorily evaporated and pot-calcined. Mercury that is present in high-level-activity TBP wastes is volatilized from the calciner pot during calcination. In the first run a large fraction of the mercury was volatilized. Material-balance data showed that it was distributed in the experimental apparatus as follows: 42% in the evaporator, 8% in the primary off-gas line, 20% in the calciner pot top, and 9% in the calcined solid. Mercury deposited between the top of the solid and the baffle, which could not be sampled, would probably account for the missing 20%. The calcined solid product had a bulk density of 0.68 g/cm^3, and its composition was 47 wt.% aluminum, 0.94 wt.% iron, 0.58 wt.% mercury, and 0.07 wt.% nitrate. The mercury concentration at the top of the solid was 1%; the remaining 9% was in the calcined solid. Temperature data showed that the solid deposited radially from the wall of the calciner toward the center. The thermal conductivity of the radially depositing solids averaged 0.92 Btu/(hr)(ft)(°F).

In the second run a condenser type mercury trap was inserted in the primary off-gas line in an attempt to collect the volatilized mercury. Steam was added to the system by means of a secondary off-gas line. The trap retained 19% of the mercury in the system, whereas 15% plated out in the calciner top and off-gas line and 29% went back into the evaporators; 33% remained in the calcined solids. The calciner solid product had a bulk density of 0.65 g/cm^3. The thermal conductivity of the cake varied from a high of 2.4 to a low of 0.27.

In laboratory-scale studies of fixation in glass solids,[3,12] aluminum borophosphate glasses were prepared which contained up to 20 wt.% Darex-waste oxides. These glasses did not become visibly devitrified on overnight annealing. Volume reductions were 2.5 to 3.8, initial softening temperatures varied from 750 to 850°C, and bulk densities varied from 2.44 to 2.74 g/cm^3.

Aluminum borophosphate glasses containing up to 25 wt.% Darex-waste oxides and 35.3 wt.% phosphorus pentoxide normally became devitrified on annealing or showed segregation. The glasses showed a wide range of properties. These varied from crystalline materials that softened at a temperature as low as 800°C to calcined solids that showed no sign of melting at 1050°C. Two of these glass products appeared to be true glasses but became devitrified to some degree when prepared in large batches.

The semicontinuous evaporation and calcination of a simulated TBP-25 waste, which was made 2.25M in sodium hypophosphite (NaH_2PO_2) and 0.25M in lead oxide (PbO) and which contained added Ru^{106} and Pm^{147}, indicated that production of the glass was accompanied by the volatilization of about 16% of the ruthenium, whereas less than 0.1% of the promethium was entrained in the off-gas. The volatilization of about 16% of the ruthenium may be compared with the 12 to 13% of ruthenium that was volatilized when 2.0M NaH_2PO_2 and 0.25M PbO were used in a similar run.[25] Thus increasing the amount of hypophosphite to 2.25M did not decrease the ruthenium volatility.

The mechanism of ruthenium volatilization under these conditions is not known. The aqueous condensate does not show the colors usually associated with ruthenium distilled from nitrate solutions. It is believed that the amount of ruthenium volatilized can, however, be considerably decreased by controlling the method of operation so as to keep the inventory of unmelted solid product always at a minimum,

thus minimizing the amount of dry solid that will be exposed on the calcination-pot walls at any given time.

No appreciable buildup of pressure is expected to develop in the storage of packaged calcined solids that have been fixed by conversion to glassy solids. This was demonstrated by heating for 30 days at 900°C a sealed stainless-steel container in which a phosphate-lead glass was prepared from the fixation of simulated TBP-25 waste solution. Actually, a vacuum that increased slowly to about 27 in. H_2O developed in the container. The vacuum was believed to be caused by the reaction of the oxygen in the air space above the glass with the stainless-steel container. Any water that may diffuse out of the molten glass must also react with the stainless steel to give oxide and hydrogen. The latter would diffuse out through the metal walls to maintain the vacuum.

The prolonged exposure of the glass in the stainless-steel container resulted in the glass acquiring a deeper brown coloration than that of the original product, probably because of the diffusion of corrosion-product oxides through the fluid melt. Metallic lead was also present in much larger aggregates than was observed in the original glass, probably as a result of the reduction of lead oxide by the stainless steel. The outside wall of the container did not appear to have suffered extensive corrosion from the long exposure to the high temperature.

Final Disposal Methods

Disposal into Permeable Formations

Early considerations of the disposal of radioactive waste into deep wells have dealt with the possible disposal of radioactive wastes containing the highest levels of activity, i.e., the fuel-processing wastes.[26] Because of their extreme hazard, it is unlikely that such wastes will purposely be discharged directly to the ground without some pretreatment to reduce the mobility of the more hazardous radionuclides.

However, ORNL is considering the application of deep-well techniques for the disposal of its high-volume low-level-activity process-waste-water streams; about 400,000 gal of this waste stream is generated daily at ORNL.[3,4] The stable chemical composition of this low-level-activity waste is essentially the same as that of ORNL tap water. Of the activity present in this waste stream, only Sr^{90} is consistently above the permissible concentration for drinking water. This waste stream is now being treated by a modified water-softening process to remove calcium and about 80% of the Sr^{90}. Clay is added to the process to remove about 85% of the Cs^{137}. The time required for the Sr^{90} to decay to the maximum permissible concentration (MPC_w) for drinking water is estimated at 200 years. This is an indication of the containment time required for the safe disposal of this waste stream.

If this deep-well method of disposal proves satisfactory for the ORNL low-level-activity wastes, it will be considered for the ORNL intermediate-level-activity wastes. This latter waste stream (10,000 gal/day) has a high salt content (about 0.5N sodium). To treat this waste, excess sodium hydroxide is added to precipitate most of the calcium, Sr^{90}, and rare earths. The supernatant is then discharged to the ground in near-surface trenches. Although most of the Sr^{90} is removed during neutralization, it remains the hazard-controlling radionuclide in the supernatant since its concentration is about 100,000 times the MPC_w. It is estimated that about 450 years would be required for the Sr^{90} in this waste stream to decay to the MPC_w. In this stream, Cs^{137} and Ru^{106} are also above the MPC_w.

When radioactive liquids are discharged into the ground, the primary means of transport of the activity is by the movement of water through the ground formation. The radionuclides follow the same paths of movement as the transporting water but move at a slower velocity because of the sorptive properties of minerals, primarily the clay minerals, which are present in the formation. Movement of the radionuclides can be predicted by describing the movement of water in the formation and correcting for sorptive processes. Although the sands that constitute good aquifers are fairly "clean," there is a sufficient quantity of clays present to give them a significant exchange capacity. For example, several California oil sands have exchange capacities[27] that range from 0.48 to 20 meq/100 g with a mean value of about 5 meq/100 g.

Precipitation reactions and filtration will provide additional restrictions on radionuclide

migration. The restricted movement of radionuclides compared to water would make it possible to use a deep aquifer as a large ion-exchange bed rather than just as a storage basin.

Calculations[3,4] based on the exchange properties of a California sand (Richfield) and the chemical characteristics of the ORNL low- and intermediate-level-activity waste streams at *p*H 7 indicate that Sr^{90} will move at a rate that is about 1% as fast as that of the low-level-activity waste solution and about 10% as fast as that of the intermediate-level-activity waste solution. However, in a high-*p*H system, the precipitation of slightly soluble calcium-strontium salts is likely, and it would result in much slower movement of the strontium than predicted from simple ion exchange in a neutral-*p*H system.

Cesium is held more strongly by the clay mineral exchangers than strontium and is present in the waste streams in relatively less hazardous quantities. Therefore its movement would contribute much less to the total hazard than would the movement of strontium. Ruthenium movement would become the hazard-controlling step in intermediate-level waste disposal only if the movement of the ruthenium were unrestricted and the movement of strontium were slowed by an additional factor of 5 by precipitation reactions.

Disposal by Hydraulic Fracturing into Shale

ORNL is continuing its investigation to determine the feasibility of disposing of liquid radioactive waste by mixing it with cement, or some other hardening agent, and then injecting the slurry deep into bedded rock through a specially constructed well.[28] The pressure developed at the bottom of the well forces the rock to fracture. Under favorable circumstances the fracture occurs along the bedding planes and thereby allows the waste-cement mixture to flow out into the rock in a thin horizontal sheet and then harden. This method may make possible the disposal of the large volumes of intermediate-level-activity wastes that are produced at ORNL.

In preliminary field experiments in 1959 (Ref. 4) and in 1961, many thousands of gallons of cement grout were pumped into a local formation at depths ranging from 300 to 934 ft. Subsequent test drillings showed that the results were encouraging toward the feasibility of disposing of wastes by this method. Another test hole has been drilled to a depth of 3263 ft near the area used for the preliminary field experiments. This test hole is at the site of a proposed disposal plant.

Waste–cement-additive mixtures[28] suitable for use in waste disposal by hydrofracture are being developed for ORNL on a subcontract by Westco Research, Fort Worth, Tex. The primary requirements for the mix are that it (1) remain sufficiently fluid for mixing, pumping, and injection and for a long enough period of time to assure the completion of these operations and (2) then harden sufficiently through hydration so that the mix will be confined in the fracture.[2,4] For plant-operating purposes the viscosity of the mix should be less than 30 poises, and the usable pumping time should be greater than 8 hr.

Preliminary tests showed that simulated ORNL intermediate-level-activity wastes and Portland cement were compatible and would form a slurry that can be pumped. The tests suggested that the waste composition will have a strong influence on slurry characteristics. The compressive strength of waste-solution–cement mixes remained relatively constant over a wide range of compositions when the grout was cured for 24 hr at 80°F. The compressive strength was much more sensitive to waste composition when the grout was cured at a higher temperature (140°F). The mixes tested contained no additives. Additives, such as bentonite, fly ash, and Pozmix, are often used to keep the cement particles suspended in the mix during setting; such additives tend to decrease the compressive strength of the set grout. As yet no minimum compressive strength requirement has been established for the hydrofracture mix.

A preliminary mix formulation with a usable pumping time of $8\frac{1}{2}$ hr and a compressive strength of 76 psi after 24-hr curing has been developed. The fluid-loss tests showed that less than 5% of the fluid will be lost in 30 min. The mix was composed of waste solution with Portland-cement additives. Four additives were chosen which would reduce fluid loss, control setting time, allow more waste to be used, and help keep cement particles in suspension. These additives were bentonite, Cemad-1, calcium lignosulfonate, and calcium chloride.

Calcined Solids Storage in Salt Mines

ORNL is continuing its studies related to the storage of packaged calcined wastes in salt mines.[15] One method under consideration for the mine disposal of these calcined wastes is to insert the canned wastes into holes drilled in the mine floor. The salt surrounding the holes will reach high temperatures because of the fission-product heat from calcined solids. The effect of these temperatures on the creep and thermal expansion of salt and the possibility of localized shattering of the salt surrounding the holes are being investigated.

Laboratory studies[3,4] have shown that unrestrained rock-salt aggregates shatter rather violently when heated to temperatures of 200 to 300°C because of the presence of small quantities of water contained in the salt crystals. If this shattering occurs in the salt *in situ*, it may result in poorer thermal conductivity and consequently increased waste temperature rise in the localized area near the heat source. Field tests to determine what effect this localized shattering will have on the temperature rise near the hole are being conducted in the Carey Mine, Hutchinson, Kans.

To obtain field data on the effects of mine depth, percentage of salt extraction, and age of mine opening on the plastic flow occurring in existing salt mines, a network of 11 new extensometer stations has been installed in the Kansas salt mines (seven in the Hutchinson mine and four in the Lyons mine). This information will be used to verify or implement theoretical calculations of room closure under various conditions of stress for the design of mine rooms to contain radioactive solids.

A feasibility study to demonstrate disposal operations in salt with radioactive heat sources was completed.[4] This experiment would use 14 canned fuel assemblies from the Engineering Test Reactor (ETR) at the National Reactor Testing Station (NRTS), Idaho, to simulate the high-level-activity solidified wastes in fission-product-decay heat generation and in level of radioactivity. The ETR fuel assemblies are being used for this experiment because the pilot-plant production of radioactive solid wastes is not expected before 1965.

Direct Liquid Disposal in Crushed Salt

A major problem in the direct disposal of high-level liquid radioactive waste is the off-gas that results from radiolytic decomposition of water and of water vapor.[4] The radiolysis may be reduced by dispersing the liquid waste through crushed rock salt which distributes the radioactive solution as a film of liquid on the surface of the granules. A liquid waste volume of 60 gal/ton and a fission-product decay cooling time of approximately three years would require 200 sq ft of mine area for adequate heat removal for each ton of uranium processed. The liquid depth would be 0.5 in. However, if this solution is poured over 6 ft of crushed salt, most of the liquid will be retained as a surface film on salt particles, and very little free solution will be found.

Laboratory studies with gamma radiation from Co^{60} indicate that the water in such a system, when subjected to temperatures about 60°C or more above ambient, tends to be moved upward, eventually collecting as a layer of liquid water on top of the salt. Very little pressure buildup associated with radiolytic-gas production is observed until the free liquid layer begins to form, at which point there is a pronounced increase in the rate of buildup. This pressure buildup can be inhibited by absorbing the water layer that is formed on an absorbent material, such as vermiculite.

Sea Burial

The results of a study of the disposal of low-level-activity packaged wastes[29,30] into deep waters of the Pacific Ocean have been issued by a subcommittee of the Committee on Oceanography of the National Academy of Sciences–National Research Council.[31,32] The subcommittee undertook to ascertain by what means and in what amounts it was feasible to dispose of radioactive material in the ocean off the West Coast of North America without curtailing the present or future use and enjoyment of the resources of the region. Its conclusions are based on assumptions and processes that emphasize the biology of the sea.

The principal site for ocean disposal off the Pacific Coast has been an explosives dumping area on the seaward side of the Farallon Islands, approximately 48 miles west of the Golden Gate. Other sites that have been used in the past are in the Santa Cruz Basin, approximately 32 miles southwest of Port Hueneme, Calif., and a site 130 miles southwest of Point Arguello, Calif. The Santa Cruz Basin site no longer is used for ocean disposal.

The subcommittee noted that, if needed, as many as 20 sites for sea disposal of low-level-activity radioactive waste could be safely established from the Mexican border to the Columbia River, with a similar number north of the Columbia River. However, AEC has no present plans to increase the number of sea disposal sites for packaged waste, since the present number of sites is more than adequate to handle the small amount of low-level wastes being disposed of at sea.[30]

Extensive environmental surveys of the Farallon Islands and Santa Cruz Basin sites have been conducted.[31] These surveys, made in 1957 and again in 1960, showed no radioactivity above natural background radiation in the water, sediments, or marine life in the disposal areas.

Extraction of Fission Products

As part of its Waste Management Program,[33] Hanford is developing processes for the extraction of long-lived heat-producing fission products from Purex-plant waste streams, formaldehyde-treated Purex acid wastes (FTW), and high-level-activity Purex neutralized waste supernatant. Ion exchange and solvent-extraction processes are being examined.

A flow sheet for the removal, purification, and recovery of cesium[T] with clinoptilolite from formaldehyde-treated, high-level-activity Purex waste (FTW) is shown in Fig. IV-7. A flow sheet for packaging the separated cesium for storage by loading it on a high-capacity synthetic zeolite is shown in Fig. IV-8. Studies on loading characteristics of cesium on clinoptilolite indicated that "residence time" or "column volumes per hour" is a valid means of extrapolating results of small columns to larger ones for this system.

Oxalic acid was used for sodium removal from the clinoptilolite column because it also removed most of the zirconium and niobium that was sorbed during the loading cycle. Cesium loss during this step was only about 0.2%. Following the oxalic acid wash, the clinoptilolite column was washed with 3 to 4 column volumes of 1*M* ammonium hydroxide (NH_4OH) to remove hydrogen ions from the clinoptilolite. This prevents gassing in the column when the ammonium carbonate eluting solution is passed through the column.

The use of a synthetic zeolite in place of the clinoptilolite is also being investigated. Equilibrium distribution coefficients (K_d) were determined for cesium, strontium, cerium, and sodium[T] in two synthetic waste solutions using a synthetic zeolite, Linde AW-400, and are as follows:

Waste	Distribution coefficients			
	Cs	Sr	Ce	Na
Purex alkaline supernate	91	1.6	4.4	1.5
FTW adjusted to *p*H 3.5	313	1.2	0.6	2.5

A run was made in which a feed of FTW adjusted to *p*H 3.5 with lithium hydroxide (LiOH) rather than sodium hydroxide (NaOH) was passed through a column filled with Linde AW-400. At a flow rate of 5 column volumes per hour, the cesium breakthrough was 2% at 260 column volumes and 50% at 360 column volumes. These may be compared with breakthroughs for cesium of 2 and 50% at 160 and 260 column volumes, respectively, for FTW adjusted with sodium hydroxide.

A flow sheet for removal of cesium[T] from high-level-activity alkaline Purex supernatant waste with Linde AW-400 (20 to 50 mesh) is given in Fig. IV-9. At a flow rate of 1 column volume per hour, a 2% cesium breakthrough was reached after passage of 26 column volumes of undiluted Purex-plant waste and 50% cesium breakthrough at 45 column volumes.

About 50% more column volumes of 2*M* ammonium carbonate were required to elute cesium from Linde AW-400 than from clinoptilolite (see Figs. IV-7 and IV-9). About 10% of the cesium from the first loading could not be eluted. However, this form of cesium did not appear to affect the capacity of the exchanger; subsequent loadings of cesium on the same exchanger showed a full capacity. Six recycles of the flow sheet have shown no detectable decrease in the loading of cesium or any other detrimental effects.

Both Hanford and Savannah River have been investigating the recovery or removal of cesium from high-level liquid wastes by scavenging with sparingly soluble metal ferrocyanides, ferricyanides, phosphotungstates, and phospho-

molybdates.[7] Hanford made a test in the Purex-plant head-end centrifuges which demonstrated large-scale operability of a nickel ferrocyanide process for removing cesium from an alkaline supernatant Purex waste.[34] A 99.6% removal of cesium from 3800 gal of waste was achieved. The precipitate was then metathesized in the centrifuges with small volumes of silver nitrate solution (which solubilizes only the cesium). This step resulted in an overall cesium recovery of 99%, a radiochemical purity greater than 99%, and a decontamination factor from sodium of 900 (the only significant cationic impurity remaining). The cesium product was of a quality suitable for cesium isolation, shipment, or for high-capacity sorption on inorganic ion exchangers for long-term storage.

Hanford continued its laboratory studies of a solvent-extraction flow sheet[35] for the recovery and separation of strontium and rare earths (particularly cerium) from FTW. This flow sheet employs di-2-ethylhexyl phosphoric acid (D2EHPA) diluted with Soltrol containing tributyl phosphate (TBP) as the extractant.

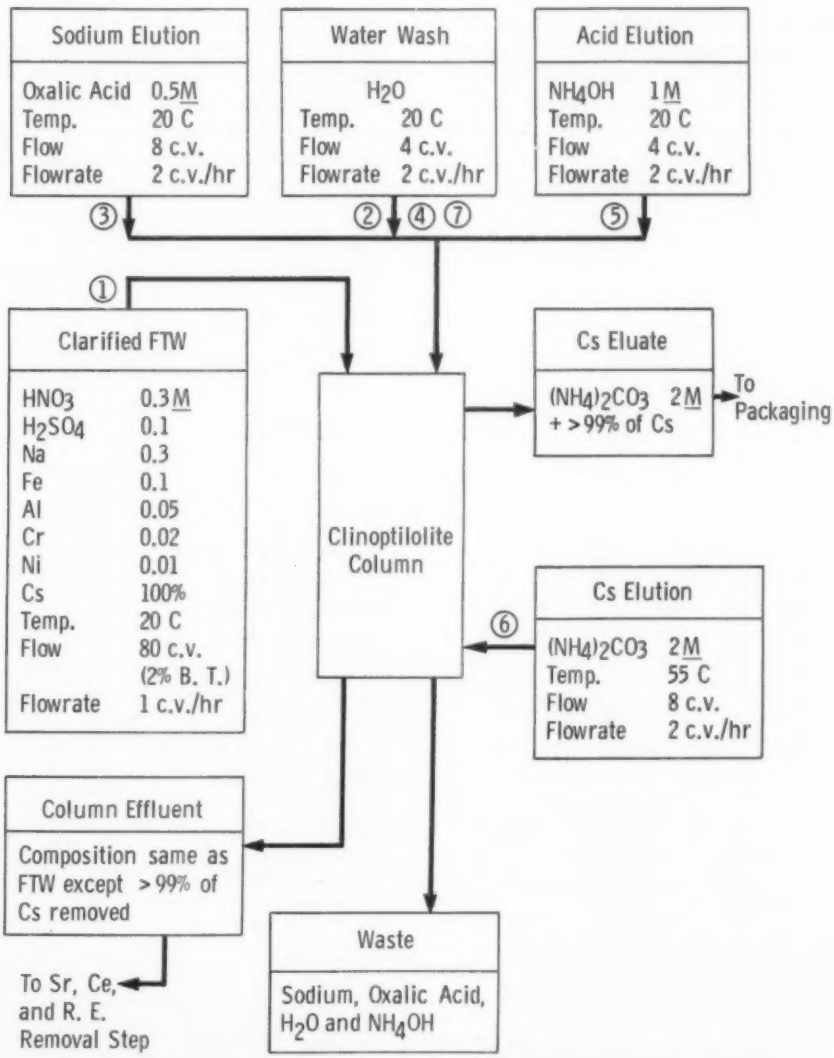

Fig. IV-7 Flow sheet for the recovery of cesium from formaldehyde-treated Purex waste.[7]

Citric acid is used in the feed to the extraction column as a buffering and complexing agent. In batch contact studies[7] the rates of formation of citrate complexes in the feed, the rates of extraction of various feed constituents, the effect of concentration of free citrate on extraction, and the effect of temperature on the rate of extraction were studied.

Hanford has initiated engineering-scale experiments to study the loading of strontium on inorganic zeolites for use in the packaging of fission products.[7] A synthetic strontium package feed was passed through a 2-in.-diameter by 36-in.-long column of $^1/_{16}$-in. Linde 4A pellets. With the feed at room temperature and a flow rate of 0.2 column volume per minute [about 1.5 gal/(min)(cu ft)], 50% strontium breakthrough occurred after 10 column volumes were processed. Decreasing the flow rate by a factor of 4 allowed about 26 column volumes to be processed to the same breakthrough. However, the results of a laboratory column experiment with the same flow rate but with a zeolite particle-size fraction of 25 to 40 mesh indicated that 31 column volumes could be processed to 50% strontium breakthrough. Further laboratory work is under way to improve the kinetics of the process.

Before inorganic zeolite beds are used for sorption, a significant amount of adsorbed and occluded gas must be removed to prevent serious gassing during the sorption step. This degassing can be achieved by prolonged soaking in distilled water (greater than three weeks) with periodic stirring to release the interstitial gas. Vacuum outgassing before placing zeolites in water or vacuum outgassing of pellets while under water can hasten the pretreatment for removing adsorbed gas.

Synthetic zeolites of high capacity and low selectivity (such as Linde 13X) are being considered as solid media on which to sorb long-lived fission products such as Cs^{137} and Sr^{90} for shipping or storage.[35] After loading, but prior to hermetic encapsulation, the zeolite bed must be exhaustively dehydrated to prevent pressurization from radiolytic decomposition of residual moisture.[7] The pressure in a con-

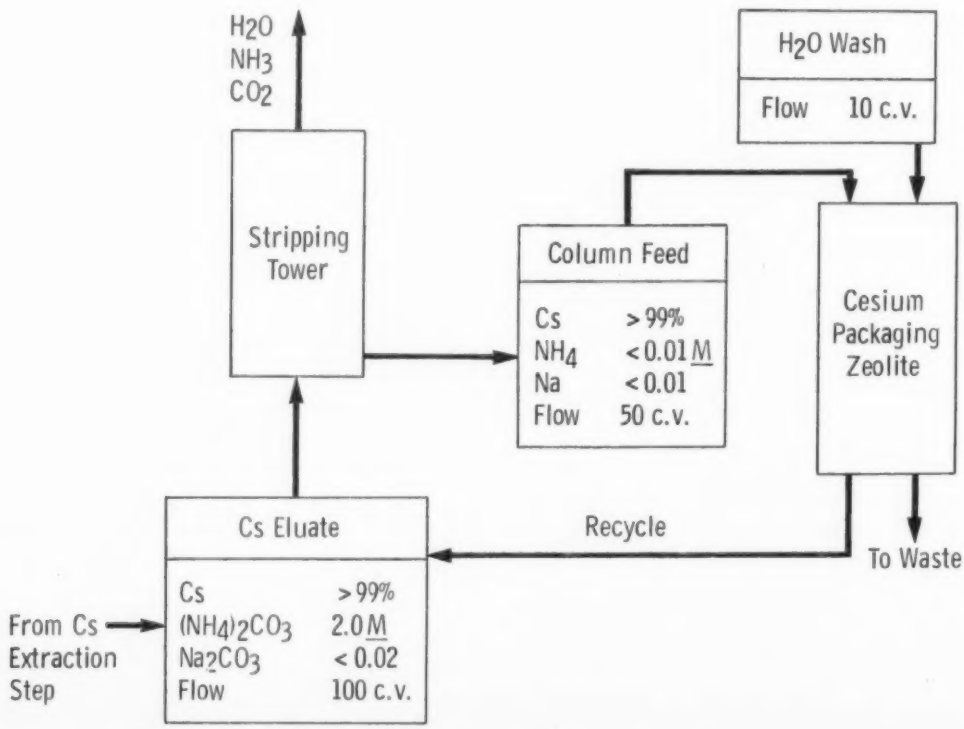

Fig. IV-8 Flow sheet for packaging of cesium.[7]

tainer from the radiolytic decomposition of a residual moisture content of the order of 0.1% may be as much as 50 psig.

Owing to the thermal properties of zeolite beds and the transient heating phenomena caused by radiolytic heat generation, gas drying was chosen for achieving low residual moisture content of zeolite beds following the sorption process. Equipment was set up to supply drying gas at 800°F (430°C) and −100°F (−73°C) dew point.

The extraction of Tc^{99} from Hanford neutralized Purex-waste-tank supernatant by anion-exchange resins was reported in a previous issue of *Reactor Fuel Processing*.[36] Roberts, Smith, and Wheelwright[37] have summarized the data from the pilot-plant-scale ion-exchange runs that were made to demonstrate the process for the extraction and purification of Tc^{99}. This process is favorable from the standpoint of waste management because the alkaline wastes can be returned to storage unchanged in any way after removal of the technetium. The results indicated that technetium can be economically recovered from neutralized Purex wastes by a single-stage ion-exchange process with overall yields greater than 80% and a technetium chemical and radiochemical purity greater than 99%.

The precipitation of cerium from trivalent rare earths in Purex-process wastes (1WW) was discussed in Hanford reports by Wheelwright and Howard[38] and Lust and Van Tuyl.[39] The process involves the precipitation of the cerium with sodium acetate and hydrogen peroxide to form cerium peroxyacetate. This precipitation technique was used to pretreat batchwise Purex-plant waste to produce a rare-earth concentrate which was then used as feed for the ion-exchange recovery[40] of Pm^{147}. The rare-

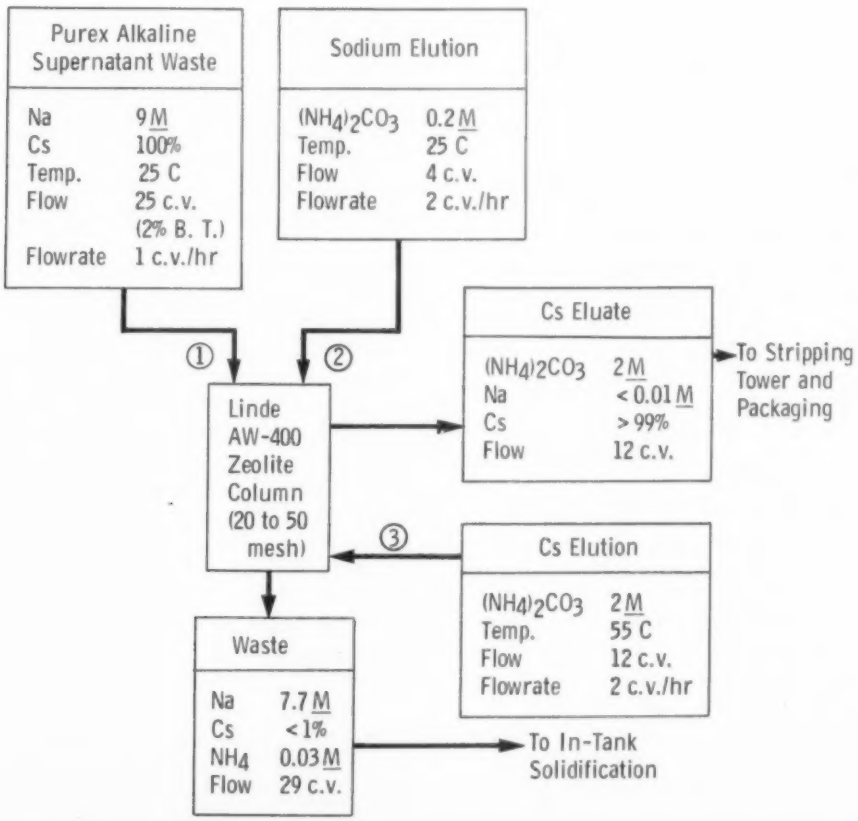

Fig. IV-9 Flow sheet for the recovery of cesium from Purex alkaline supernatant waste.[7]

earth concentrate contained about 250,000 curies of cerium and 50,000 curies of promethium. After the cerium was precipitated, the resulting supernatant contained about 70% (34,000 curies) of the original amount of promethium and only about 7% (17,000 curies) of the original amount of cerium.

Several reports[41–43] have become available which present information on programs for the testing of shipping containers[44] and on the consequences of accidental releases of high-level radioactive materials during shipment. In a recent conference, current testing programs of radioactive material shipping containers and related items were discussed.[41] At this conference, papers were presented which outlined work in progress on operations research studies of potential accidents, consequences and costs of accidents, fire testing of containers, heat-transfer problems, and unique licensing problems. The container testing programs conducted by Brookhaven National Laboratory, E. I. du Pont de Nemours & Co., Inc., with the Franklin Institute and Lehigh University, Hanford Atomic Products Operation, ORNL, the Sandia Corporation, and the United Kingdom Atomic Energy Authority were reviewed. AEC technical transportation problems in establishing standards, as well as operational safety features, for the shipment of isotopes and other radioactive materials were discussed.

Morgan, Knapp, and Thompson[42] at Johns Hopkins University have evaluated the possible consequences of accidental releases of high-level radioactive materials during shipment by truck. In describing the hypothetical accidents, it was envisioned that during shipment: (1) one Materials Testing Reactor (MTR) fuel element with its cooling waters would be released from its cask or (2) portions or all of approximately 500 gal of the liquid processing wastes would be released from the shipping container. Situations leading to a truck accident are visualized, unit costs for remedial operations are cited, and economic losses are established as a result of business shutdowns. The following items, pertinent to cost analysis, were reviewed: transportation practices and shipping containers, ability of large metropolitan areas to handle accident situations, characteristics of the high-level wastes, fate of radioactive materials in the environment, removal of radioactive nuclides by water-treatment facilities, and decontamination procedures.

Large quantities of Cs^{137} and Sr^{90} are shipped by rail from Hanford to ORNL. The possible consequences of an accidental release of either cesium or strontium during shipment by rail and the associated potential dangers to the public and its environment are the subject of a report by Watson, Fuquay, Junkins, and Zahn[43] at Hanford.

Other Literature

ORNL has completed an eight-volume bibliography on nuclear reactor fuel processing and waste disposal.[45,46] The complete collection consists of some 7000 abstracts, nearly all from *Nuclear Science Abstracts*, representing books, bibliographies, symposia, journals, and contractors' topical reports. Most of the material dates from the 1955 Geneva Conference to October 1962. The titles of the individual volumes in the set are as follows:

Volume 1	Chemistry and Physics of Important Elements
Volume 2	Fission Product, Poison, and Radioisotope Removal
Volume 3	Fissionable Material Recovery
Volume 4	Hazards and Protection
Volume 5	Plants and Equipment
Volume 6	Process Chemistry and Engineering
Volume 7	Surveys (General)
Volume 8	Waste Treatment and Disposal

AEC has compiled a 152-page supplemental bibliography[47,48] of 874 references to reports and published literature in the field of radioactive-waste processing and disposal. The references have been taken from *Nuclear Science Abstracts* and cover the period from June 1960 through May 1962.

The International Atomic Energy Agency (IAEA), Austria, has published two reports concerned with radioactive wastes. The one report by Mawson[49] covers the development of techniques for the processing, rather than the disposal, of gaseous, liquid, and solid wastes between 1955 and 1960. The other report contains the findings and recommendations of an *ad hoc* panel[50,51] that studied the technical and scientific problems connected with the disposal of radioactive waste into the sea.[52]

The U. S. Geological Survey,[53] Department of the Interior, has made a comprehensive litera-

ture survey of clay minerals and other naturally occurring silicate minerals which exhibit the phenomenon of ion exchange. The role of mineral ion exchangers in the treatment and disposal of radioactive wastes is also discussed.

AEC has published a guide[54] that contains recommended procedures for the inspection, storage, handling, and installation of high-efficiency particulate air filter units. The precautions and recommendations in this publication are based on actual experience and current development.[55]

First and Silverman[56] at the Harvard School of Public Health have analyzed the cost and effectiveness of air-cleaning systems in a review article in *Nuclear Safety*. Data on cost-evaluation practices, on cost analysis of prefilter and AEC type filter installations, and on effectiveness of air-cleaning performances are presented.

The Bureau of Mines[57] has developed an incinerator (BOMAEC-30) for disposing of solid, combustible wastes containing low-level radioactivity. The incinerator can handle about 30 lb of rubbish and sawdust per hour, using 100% overfire air and a negative pressure during operation. The solid residue, mostly ash, that results from incineration is $\frac{1}{20}$ to $\frac{1}{10}$ of the volume of the original waste.

Dennis and Silverman[58] at the Harvard School of Public Health have presented, at the Seventh Air Cleaning Conference (October 1961), a review of radioactive waste incinerator design and operational experience in the United States. Incinerator operating experience at several AEC sites, basic design requirements, operational problems, and economic considerations were discussed. Performance data were also given for two incineration systems currently in use at the Dow Chemical Co., Rocky Flats, Colo., and at the General Electric Company, San Jose, Calif. Basic research on institutional type incinerators (Bureau of Mines and Harvard Air Cleaning Laboratory) was also described.

The reader is also referred to a review article on waste disposal by incineration which appeared in *Nuclear Safety*.[59]

Corrosion in Waste Processing

The susceptibility of low-alloy steels to stress cracking in neutralized or alkaline synthetic Purex waste is being investigated at Hanford.[60,61] Large weldments (3 by 3 ft by $\frac{3}{8}$ in.) were exposed to two environments, 50% sodium nitrate and 6 M sodium nitrate–0.2 M sodium nitrite at 90°C. Three weldments in the first environment cracked during the interval between 60 and 90 days of exposure. One weldment (out of a total of eight) cracked in the second environment after 42 days of exposure. The construction material was ASTM 282 Grade C steel (semikilled 0.12 carbon), welded with 6010 welding rod. Additional exposures were made in 50% sodium nitrate–1 M sodium nitrite solution to determine the effect of nitrite on stress-cracking suscepti-

Table IV-2 CORROSION IN ICPP ALUMINUM-PROCESS RAFFINATE STORAGE TANKS[16]

(Conditions: Temperature, 25 ± 5°C)

Type of raffinate	No. of tanks	No. and type of specimens*	Exposure time, year	Av. corrosion rate, mils/month	Results of examination
1st cycle TBP	2	12 hoops,† S.S. 304L	2.75	0.004	Only slight etching; no pitting or grain-boundary attack
1st cycle TBP	2	12 hoops,† S.S. 304L	2	0.003	Only slight etching; no pitting or grain-boundary attack
1st cycle hexone	1	1 welded pipe, 20 ft long, S.S. 348	7	<0.001	Uniform light etch; no pitting or intergranular attack
2d and 3d cycles‡ hexone	1	6 hoops,† S.S. 304L	2.75	0.004	Heavy etching; pits 5 mils deep

*Corrosion specimens and storage tanks are of the same stainless-steel type.

†Welded hoops of schedule-40 pipe, 1 in. high.

‡Corrosive decontaminating agents are blended with the column raffinates in this tank.

bility. Results of these tests are not yet available.

Measurement of corrosion rates for underground stainless-steel storage tanks containing high-level radioactive wastes is a continuing program at the ICPP. Specially prepared corrosion-test specimens are removed from the tanks periodically, and measurements are made to estimate corrosion rates of the tank. Results of recent measurements[16] are shown in Table IV-2. In general, corrosion of the stainless-steel tanks (types 304L and 348) used for storage of aluminum fuel-processing wastes was considered to be negligible, but measurable. Continued storage of current wastes in existing tanks does not appear to be limited by corrosion.

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Production of Uranium Trioxide

Continous Calcination of Uranyl Nitrate

The first large-scale method of producing uranium trioxide was by batch calcination of uranyl nitrate in agitated denitration pots. This method has several disadvantages, chief of which are variability in product quality among successive batches and high maintenance costs due to the short life expectancy of the stainless-steel pots. Failure of the reactor shells is frequent because of the repeated thermal cycling that is an inherent feature of the process. The severity of the thermal effect is increased by the presence of an insulating crust that collects between the inner surface of the reactor and the agitator blade. These disadvantages have prompted the development, by National Lead Co. of Ohio, Fernald, Ohio, of a continuous-pot denitration system that has proved capable of sustained operation at production rates greater than those obtained in the batch process.[1] A schematic drawing of the continuous denitration pot has appeared in a previous Review.[2]

The uranyl nitrate feed to the denitration pot is a molten salt whose composition is approximately that of $UO_2(NO_3)_2 \cdot 3H_2O$. The temperature of process vessels and lines containing the feed must be controlled between 113 to 121°C to prevent both crystallization and premature decomposition. The density of uranyl nitrate at this temperature level is about 2.5 g/cm^3; the uranium content is about 10.1 lb/gal. Densities up to 2.6 g/cm^3 may be used, but care must be taken to prevent the formation of solids in the feed lines. It is expected that with improved temperature control the density of the feed stream could be increased to 2.7 g/cm^3 (11.5 lb of uranium per gallon). At feed densities below 2.35 g/cm^3, the free-flowing character of the uranium trioxide product is lost and operation of the continuous-pot reactor becomes impossible.

In the refinery process at National Lead Co. of Ohio, the purified uranyl nitrate from the extraction plant is treated with ammonia to reduce the nitric acid content. The addition of ammonia is controlled so that the *p*H of the treated stream is 2.2 to 2.3 or below; depending on process conditions, the ammonia may range between 10,000 to 50,000 ppm (uranium basis). Above a concentration of about 12,000 ppm ammonia, the crystallization temperature of the system exceeds that of pure uranyl nitrate, and the feed to the denitration pot contains small amounts of solids. At ammonia concentrations above 20,000 ppm, operation of the process is impossible due to excessive crystallization in the feed stream unless the feed is diluted to a density of 2.4 g/cm^3. In the processing of feed streams containing ammonia in concentrations in excess of 10,000 ppm, sulfate (1000 ml of concentrated H_2SO_4 in 275 gal of uranyl nitrate) must be added to the feed stream to ensure the production of spheroidal uranium trioxide. In the absence of sulfate, the oxide product appeared as a light-yellow fluffy material that could not be processed through the system.

The molten uranyl nitrate is fed by gravity to the denitration pot from a storage tank. The feed is introduced into the pot by means of two steam-cooled feed tubes that extend beneath the surface of the uranium trioxide bed. Temperature of the bed is maintained at 246 ± 3°C. The pot is heated by gas-fired radiant burners arranged in three concentric rings about 20 in. below the pot bottom. Heat input is controlled to maintain the temperature of the bottom of the pot at 704 ± 3°C. The oxide product, which dis-

charges from the reactor through a central overflow pipe, is in the form of free-flowing spherical particles varying from 100 to 500 μ in diameter.

Production rates of 570 lb of UO_3 per hour were obtained in demonstration runs, and for short intervals a maximum rate of 750 lb of UO_3 per hour was achieved. During these periods of high productivity, an overall heat-transfer coefficient of 20 Btu/(hr)(sq ft)(°F) was calculated.

The product, which was determined to be the gamma polymorph of uranium trioxide (γ UO_3), contained approximately 0.42% nitrate, 0.26% water, and negligible quantities of U_3O_8. The reduction rate of the UO_3 from the continuous-pot process to uranium dioxide is relatively slow compared to material made by batch denitration. This factor may be overcome by grinding[2] or by a reduction-oxidation-reduction cycle.[3,4]

Properties of Uranium Trioxide

Uranium trioxide is an important intermediate in the commercial production of uranium dioxide and uranium tetrafluoride. Uranium tetrafluoride is prepared by a high-temperature reduction of uranium trioxide to uranium dioxide followed by hydrofluorination to uranium tetrafluoride. The reactivity of uranium dioxide toward hydrofluorination depends on its physical properties (particle size, porosity, and surface area) which, in turn, are governed by the origin and structure of the parent uranium trioxide. At least six polymorphs (five crystalline phases and an amorphous phase) of uranium trioxide are known to exist. Cornman[5] has investigated the preparation and characterization of the polymorphic forms of uranium trioxide. Five crystalline polymorphs and an amorphous form of uranium trioxide were prepared by the thermal decomposition of the hydrates of uranyl nitrate, uranium trioxide, and uranium peroxide. In a subsequent study, Cornman[6] investigated, in a series of thermobalance tests, the extent of conversion of the six polymorphs of uranium trioxide to uranium tetrafluoride under two sets of conditions: (1) reduction to uranium dioxide with hydrogen at 500°C followed by hydrofluorination at 550°C and (2) reduction at 900°C followed by hydrofluorination at 550°C. The conversion behaviors of the polymorphs were compared by measuring the extent of hydrofluorination after a given reaction time.

The beta and zeta crystalline forms of uranium trioxide were more reactive than the other polymorphs. Beta UO_3 was prepared by rapid denitration of uranyl nitrate hexahydrate (UNH) at 500°C. Denitration of UNH at 425°C in the presence of 0.6 wt.% sulfamic acid produced ζ UO_3. At 500°C the reductions of β, ζ, and amorphous polymorphs were more rapid than the reductions of the other forms. At 900°C the reductions of the six polymorphs proceed too rapidly to allow the detection of any significant differences in rates among the polymorphs. The time required for complete reduction at 500°C decreased with an increase in surface area of the polymorphs. After reduction at 500°C the products from the β and ζ polymorphs hydrofluorinated more rapidly than those from the other polymorphs. This behavior of the β and ζ polymorphs is probably related to the observation that the surface areas of these two polymorphs increased during reduction, whereas the surface areas of the other polymorphs decreased during reduction. It is suggested that a significant improvement in the commercial-scale production of uranium tetrafluoride might be realized by taking into account the unusual properties of the β and ζ polymorphs of uranium trioxide if the results of these laboratory tests hold on a plant scale.

Dell et al.[7] have made a kinetic study of the reaction of hydrogen fluoride with uranium trioxide and with U_3O_8. At temperatures between 200 and 450°C, the reaction between uranium trioxide and hydrogen fluoride to produce uranyl fluoride proceeds at a rate that is virtually independent of temperature but is markedly dependent on the texture of the uranium trioxide. The reaction between hydrogen fluoride and U_3O_8 produces a solid product containing $2UO_2F_2 + 1UF_4$. This reaction has an activation energy of 5 ± 1 kcal/mole.

Several tests[7] were performed to ascertain the nature of the oxide formed by the hydrolysis of the fluorides produced in hydrofluorination of U_3O_8. A sample of U_3O_8 was completely hydrofluorinated to $2UO_2F_2 + 1UF_4$ at 310°C. Hydrolysis of the products was effected by heating for 90 min in wet nitrogen at 470°C. The hydrolysis product was observed to be crystalline U_3O_8 rather than a two-phase mixture of uranium trioxide and uranium dioxide. In a similar test in which the hydrolysis was conducted at 500°C, a form of U_3O_8 was produced which was very reactive toward hydrofluorination.

Production of Uranium Dioxide

Conversion of Uranium Hexafluoride to Uranium Dioxide

High-density spheroidal uranium dioxide particles, suitable for application in dispersion or vibratory-compacted or swaged fuel elements, have been prepared at Argonne National Laboratory (ANL) directly from uranium hexafluoride in a continuous, single-step operation employing fluidization techniques.[8,9] Uranium hexafluoride is fed continuously into a fluidized bed of granular uranium dioxide and reacted with a mixture of steam and hydrogen which serves as the fluidizing medium. This reaction actually proceeds by a vapor-deposition process in which the newly formed solid products coat the particles of the bed.

Process development studies have been conducted in a 3-in.-diameter cone-bottom Monel column using a 6-kg bed of uranium dioxide (equivalent to an 8-in. static bed height). The operating procedure involved alternate periods of hexafluoride feed time followed by a period in which only steam and hydrogen were used to remove residual fluoride from the particles. Hexafluoride feed rates ranged from 10 to 34 g/min, and the steam rates were from 0.1 to 12.6 times the stoichiometric requirement (based on the reaction $UF_6 + H_2 + 2H_2O \rightarrow UO_2 + 6HF$). The hydrogen rates were 10 to 20 times the stoichiometric requirement. The uranium hexafluoride on-time period ranged from 15 min to 1 hr. Fluoride cleanup periods were usually of ½-hr duration. Product was removed semicontinuously; after each fluoride cleanup period, a quantity of product was withdrawn such that the bed weight remained approximately constant.

The following effects have been observed with respect to the density of the uranium dioxide particles:

1. Higher bed temperatures, 700°C as compared with 650°C, produced a higher density material, 9.7 to 9.8 g/cm^3 as measured by mercury displacement.
2. Higher density particles were obtained in tests in which the steam excess was in the range 0.75 to 1.4 times the stoichiometric requirement. With smaller or larger quantities of steam, lower density material was produced.
3. Decreasing the uranium hexafluoride feed rate from 34 to 17 g/min increased the particle density from 9.1 to 9.5 g/cm^3.
4. The length of the uranium hexafluoride on-time period within the range of 15 to 30 min had no apparent effect on particle density.
5. The depth of penetration of the uranium hexafluoride feed nozzle into the bed affected the density of the uranium dioxide particles. The use of a long nozzle, extending vertically about 3¾ in. into the bed, resulted in a product of higher density than that obtained when a short nozzle, extending only ¾ in. into the bed, was employed.

Residual fluoride content of the uranium dioxide product consistently ranged between 200 and 300 ppm. Nickel content of the product ranged from 17 to 30 ppm, thereby indicating low corrosion rates in the Monel reactor.

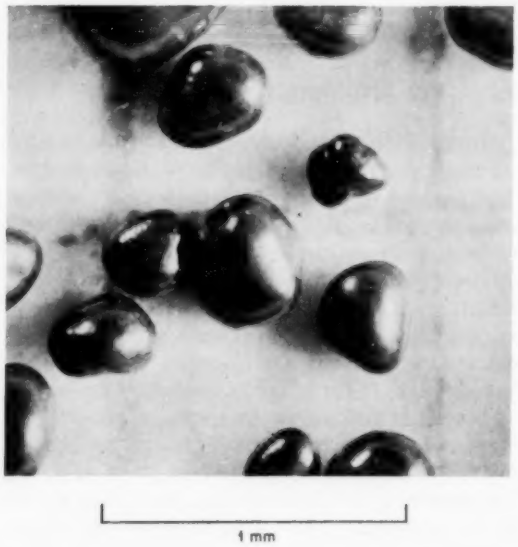

Fig. V-1 Dense uranium dioxide particles as produced in the fluid-bed reactor.[9] The final particle density was 9.3 g/cm^3.

Typical material, as produced in the fluid bed, is shown in Fig. V-1, which illustrates the smooth, spheroidal appearance of the particles. Measurements of pore-size distribution of the uranium dioxide product particles showed that most of the pores were less than 0.4 μ in diameter and that a significant portion was below

0.06 μ in diameter. A high-temperature firing for 2.5 hr in hydrogen at 1600 to 1725°C resulted in elimination of much of the fine pore structure and produced a more dense material. Final particle densities ranged from about 10.4 to 10.6 g/cm^3 or about 95 to 96.5% of theoretical density regardless of the particle density prior to firing.

Reduction of Uranium Trioxide with Ammonia

Recently, increasing costs of maintenance of ammonia dissociators and hydrogen off-gas system have prompted interest at National Lead Co. of Ohio[10] in the use of undissociated ammonia in the reduction of uranium trioxide to uranium dioxide. It is reasoned that, if the ammonia in the fluid-bed reactors does not dissociate appreciably, it would be possible to employ wet scrubbing, a comparatively trouble-free process, in the off-gas system.

A series of laboratory tests was made to evaluate the use of undissociated ammonia in the reduction of uranium trioxide currently being processed at National Lead Co. of Ohio. The results of these tests indicate that, although uranium trioxide can be reduced to uranium dioxide by ammonia at 500°C, the reduction rates with ammonia are slower by a factor of approximately 1.5 than with hydrogen at 500°C. Essentially no dissociation of ammonia was observed during reductions at temperatures up to 600°C. Results of preliminary tests indicate that the rate of hydrofluorination of ammonia-reduced oxide to uranium tetrafluoride is somewhat faster than that of hydrogen-reduced oxide.

The kinetics and mechanism of ammonia reduction of uranium trioxide appear to be considerably different from those of hydrogen reduction. Since no dissociation of ammonia occurs, the reaction involves the ammonia molecule itself rather than the hydrogen resulting from a prior dissociation process. The reaction apparently proceeds by way of a catalytic decomposition of ammonia on the surface of the oxide with the reduction being effected by atomic hydrogen. The reduction was observed to take place in two distinct steps with an abrupt change in rate occurring at a composition approximating $UO_{2.56}$. The first part of the reaction is faster with ammonia than with hydrogen; the second part is slower. The lower overall reduction rate with ammonia is attributed to the lower rate obtained in the second step of the reduction. The phase change occurring at $UO_{2.56}$ evidently retards the dissociation process throughout the second part of the reaction.

Characterization of Uranium Dioxide

Most water-cooled water-moderated nuclear power reactors utilize sintered uranium dioxide as the fuel. This fuel must be of high density (>93% theoretical density) to assure dimensional stability of the fuel and a high degree of fission-gas retention. Uranium dioxide powders are produced by several different methods, and the powders are currently evaluated for use in sintered fuels by a series of performance tests involving pellet fabrication under a specific set of conditions. These performance tests are laborious and costly, and the results are often greatly affected by the manner in which the tests are made. As a consequence, considerable attention has been directed toward the development of test methods for uranium dioxide powder which would measure certain physical attributes of the powder as an index of sinterability, thereby eliminating the need for performance tests.

Driear[11] has correlated certain characteristics of uranium dioxide powder with sinterability and has observed that the specific surface, as measured by a modified Brunauer-Emmett-Teller (BET) method, is the most important powder characteristic. From this method the sinterability of the powder can be predicted once a fixed powder-making process and a fixed sintering process have been established.

The size and size distribution of pores appear to have a marked influence on the sintering behavior of ceramic powders.[12] A critical range of pore diameters (not yet completely defined) exists within which maximum sintered densities may be achieved.

Carpenter et al.[13] have described a program conducted at United Nuclear Corp. which involved the characterization of 12 different uranium dioxide powders and the correlation of the powder properties with sinterability. Definite relations have been shown to exist between a number of uranium dioxide powder variables and sintering response; however, the correlations are not sufficiently definitive to provide a basis for uranium dioxide powder specifications.

The effect of ammonium diuranate (ADU) precipitation conditions on the characteristics

and sintering behavior of uranium dioxide has been studied by Ainscough.[14,15] No definite correlation was found betwen the condition under which ADU is precipitated and the sintered densities of uranium dioxide compacts. The differences between ADU precipitates are, to a large extent, leveled out during subsequent processing with most of this occurring during calcination. ADU precipitates that differed markedly in surface area produced, after calcination to U_3O_8 in argon at 700°C and reduction in hydrogen at 700°C, uranium dioxide of similar specific surface. Ainscough concludes that the calcination temperature is the principal factor in determining the surface area of the uranium dioxide product.

Doi et al.[16] have examined in detail the major factors affecting the physical properties of uranium dioxide by following the change of ADU to uranium dioxide powder. It was observed that the temperature of ADU calcination is a major factor in determining the surface area of uranium dioxide prepared by reduction of U_3O_8. In the case where ADU is initially calcined to uranium trioxide prior to reduction, the specific surface of uranium dioxide is markedly dependent on the reduction temperature and on the surface properties of the uranium trioxide. The progress of free sintering of uranium oxide particles during calcination and reduction shows marked dependence on the character of ADU. The influence of the character of the starting ADU is observed in the densification of uranium dioxide particles at reduction temperatures as high as 1700°C.

Moorthy and Rao[17] have observed a considerable variation in the characteristics of uranium dioxide powder derived from organic uranyl compounds. The compounds that were compared in this study were ammonium diuranate, uranyl acetate, uranyl benzoate $[UO_2(C_7H_5O_2)_2]$, uranyl 8-hydroxyquinolinate $[UO_2(C_9H_6ON)_2]$, and uranyl tannate $[UO_2(C_{14}H_9O_2)_2]$. Comparison of the uranium dioxide prepared from these compounds showed that the compound with the largest amount of organic matter associated with each uranium atom yielded uranium dioxide with the finest crystallite size.

The preparation of high-density material by sintering required much lower sintering temperatures with powders composed of small crystallites than with powders composed of large crystallites.[17] With 0.013-μ crystallites of uranium dioxide, derived from uranyl tannate, sintering at 1100°C in hydrogen resulted in material of near theoretical density. With 0.04-μ crystallites of uranium dioxide from ADU, sintering at 1500°C in hydrogen was required to obtain material of comparable density. The atmosphere during sintering of uranium dioxide has a pronounced effect on the crystallite growth of the oxide. The rate of crystallite growth was more rapid for fine crystallite material in hydrogen than in argon. Since uranium dioxide obtained from uranyl tannate can be sintered in hydrogen to 98% of the theoretical density in 3 to 6 hr at temperatures between 1100 and 1300°C, this method appears to have commercial potentialities for fuel development.

Preparation of Uranium Carbide and Other Refractory Materials

Uranium Monocarbide

By comparison with other refractory compounds of uranium, the monocarbide is particularly attractive as a nuclear fuel because of its high uranium density, high thermal conductivity, low parasitic neutron capture, and good irradiation resistance at high temperatures. Dense uranium monocarbide appears to be well suited for use in sodium- and organic-cooled reactors. Battelle Memorial Institute (BMI) has compiled[18] salient data on the properties of fuel materials for high-temperature reactor concepts. This compilation includes, in addition to data on uranium monocarbide, information on uranium alloys, ceramic compounds, dispersions, and cermets. Chubb and Dickerson[19] have reviewed the properties of uranium carbides with particular reference to their application as nuclear fuels.

The preparation of uranium monocarbide by reaction of uranium metal powder with graphite is being studied extensively. Brown and Stobo[20] have investigated the factors affecting the final density of uranium monocarbide compacts prepared by direct combination of the elements. The procedure involved cold pressing of a mixture of uranium and graphite powders, reacting the mixture at 1050°C, and sintering the reaction product at temperatures up to 2000°C. Uranium monocarbide compacts were produced with

densities above 80% of theoretical and with about twice as much closed as open porosity. The results of this study indicate that the oxygen content of the uranium-carbon compacts is of prime importance in determining the final density of the monocarbide. High oxygen content leads to the formation of a large number of closed pores in the product which are not eliminated by high-temperature firing. High-density product was achieved with 4.5 to 4.8 wt.% carbon; at higher carbon contents there was a progressive and significant decrease in density.

Regan and Hedger[21] at Harwell have observed that uranium monocarbide produced by rapid reaction sintering of the elemental powders at modest temperatures (1100°C) has a density higher than that normally obtained by direct sintering of uranium carbide powder at 1900 to 2100°C. The success of the process depends largely on the rapid heating of the metal-plus-carbon compacts to 1100°C. Slow heating induces about 20% porosity in the final compacts, whereas rapid reaction sintering produces a carbide containing about 10% porosity. The reaction between uranium and carbon is exothermic, and the temperature of a compact plunged into a furnace at 1100°C rises rapidly to approximately 1400°C. During the period when the compact temperature exceeds that of the furnace, liquid uranium is present and contributes to the sealing of the pores. The melting of uranium apparently leads to the formation of the large amount of closed porosity in the product. Uranium monocarbide specimens produced in preliminary tests had a density of 12.3 ± 0.1 g/cm^3 (90% of theoretical), 2% open porosity, and 8% closed porosity.

Uranium Nitride and Boride

Uranium nitride has many favorable characteristics that make it potentially attractive as a nuclear fuel material. In powder form it is not nearly so reactive with the atmosphere as uranium monocarbide. Bulk uranium mononitride is stable in boiling water and resistant to steam[22] at 260°C. Kerr[23] has prepared a survey of the published literature on the uranium-nitrogen system, which includes a review of methods of synthesis and fabrication of compounds and tabulations of physical-chemical properties. Data on the physical properties of uranium mononitride have been compiled by Endebrock[18] of BMI.

Uranium mononitride may be prepared[22] by heating uranium metal in pure nitrogen at 850°C to form U_2N_3 and then decomposing the U_2N_3 in a vacuum to form the mononitride. X-ray diffraction analyses showed that the powder produced by this process was uranium mononitride free of U_2N_3. Dense uranium mononitride bodies are not easily obtained by vacuum sintering. It appears that uranium mononitride dissociates during vacuum sintering at 1800°C into nitrogen and free uranium. High-density (96% of theoretical) uranium mononitride bodies have been prepared[22] by hot pressing at 1450°C. Molinari[24] also obtained dense uranium mononitride by hot-pressing techniques.

Preparation methods and properties of uranium diboride and uranium tetraboride have been studied by Matterson et al.[25,26] to provide a preliminary evaluation of these compounds for use as nuclear fuels. The borides were prepared by blending the requisite amounts of crystalline boron and uranium, pressing the blend into compacts, and reacting the mixture at 1000°C in an argon atmosphere. The uranium diboride product contained 1 to 5% uranium tetraboride and 1 to 2% uranium dioxide, whereas uranium tetraboride contained 1 to 2% uranium dioxide as the major impurity.

Dense bodies could not be obtained by sintering of the borides in vacuum because of loss of boron. When heated at 2000°C in vacuum, the borides tended to lose boron and thus produce the lower boride and the metal. High-density compacts were obtained by hot pressing at 1800°C under a pressure of 2 tsi. Several tests were made[26] to ascertain the nature of the product formed when uranium boride was hot pressed with uranium monocarbide. X-ray data have indicated that uranium borocarbide (UBC) is a product of the reaction. Attempts to prepare this compound from the elements yielded a product that was only 60% pure.

Plutonium-Containing Ceramics

Interest in fast reactors has revealed a need for a breeder type fuel. Various compositions of plutonium, uranium, and their compounds are being studied for this purpose. Of considerable interest for this type of application is a solid solution of plutonium monocarbide in uranium monocarbide. Ogard et al.[27] have prepared carbon-deficient uranium monocarbide–plutonium monocarbide solid solutions by sintering

mixtures of uranium dioxide, plutonium dioxide, and graphite at 1450 to 1850°C in vacuum. Substances other than the uranium monocarbide–plutonium monocarbide solid solution were not detected by X-ray diffraction or metallography. Single-phase solid solutions were prepared in the range 35.9 at.% uranium–15.4 at.% plutonium to 46.1 at.% uranium–5.1 at.% plutonium by sintering oxide mixtures with graphite. Pellet densities up to 12.85 g/cm^3 (94.5% of theoretical) have been achieved by resintering the solid solution. It has been observed by Harrison et al.[28] that solid solutions of 15 wt.% plutonium monocarbide in uranium monocarbide can be sintered at 1550°C to densities greater than 95% of theoretical provided that the carbide is milled to a fine powder and protected from oxidation at all stages of the fabrication process. Milling to a mean particle size of less than 4 μ is essential for obtaining products of high sintered density.

From previous experiments[21] it is known that dense uranium monocarbide may be prepared by heating the metal-graphite compacts rapidly to 1100°C. This technique has been extended by Regan and Isaacs[29] to the preparation of uranium monocarbide–plutonium monocarbide solid solutions by sintering uranium and graphite in the presence of plutonium monocarbide. It was observed that the particle size of the plutonium monocarbide additions had a noticeable effect on the sintered density of the product. In general, the addition of 15 wt.% plutonium monocarbide of particle size larger than 175 μ produced sintered densities in the range 12.3 to 12.5 g/cm^3. Addition of plutonium monocarbide with a particle size smaller than 175% produced a marked decrease in density.

The preparation of single-phase plutonium monocarbide by carbon reduction of plutonium dioxide does not appear to be practicable.[27,30] Plutonium sesquicarbide (Pu_2C_3) is consistently formed in amounts ranging from 20 to 50 at.%. Arc melting of the PuC-Pu_2C_3 product eliminates the sesquicarbide and results in a single-phase plutonium monocarbide of 98.5% theoretical density.[27]

Arc melting of massive plutonium metal and graphite has proved successful in preparing single-phase plutonium monocarbide.[30] The preparation of plutonium monocarbide is also being investigated at ANL.[31] At ANL, plutonium metal is melted in a bare graphite crucible. The reaction becomes rapid above the PuC peritectic temperature (1654°C). Metallographic examinations of the carbide product have shown a PuC matrix with small quantities of plutonium sesquicarbide and no evidence of free plutonium. No metallographic samples have shown single-phase plutonium monocarbide. Direct melting appears to be a feasible method for producing large quantities of near-stoichiometric plutonium monocarbide. Reactions with charges as large as 350 g have been successful, and no problems are anticipated in scaling up to 1-kg batches.

Production of Uranium Metal Powder

There is considerable demand for uranium metal powder as a primary material in the production of uranium compounds by powder metallurgy. Powdered uranium metal is usually employed in the manufacture of uranium carbide, uranium nitride, and cermets. A process in which uranium dioxide is reduced by calcium metal has been developed for the production of uranium metal powder directly at a rate of 10 kg/day.[32]

Uranium dioxide feed is prepared by hydrogen reduction of uranium trioxide. The product is heat-treated at 1100°C to induce low reactivity in air. To ensure homogeneity of particle size, all +80-μ agglomerates are removed from the oxide powder by grinding and sieving. Calcium metal is in the form of granules 0.3 to 2 mm in size. The calcium and uranium dioxide are mixed in a mole ratio of 3 to 1 and pressed into pellets 8 cm in diameter by 3 cm in height.

The reduction of uranium dioxide is carried out in a closed vessel under a controlled atmosphere of argon. The pellets are placed on a calcium oxide disk within the reduction vessel. The reaction is initiated by raising the temperature of the system to 800°C. Once started, the reaction proceeds without further heating since the heat of reaction is sufficient to increase the temperature above the melting point of uranium. Upon completion of the reaction, the mixture is allowed to soak for 5 hr at a temperature of 1100°C. The uranium metal product appears as small spheres within the refractory skeleton of calcium oxide.

The lime sinter is crushed and treated with 4N acetic acid at a temperature of 0 to 3°C. Lime and excess calcium are dissolved in the

acid while the metal remains in suspension. The metal powder is recovered by filtering the solution, followed by washing with cold 4*N* acetic acid and ice water. Superficial oxide on the metal surface is removed by dilute sulfuric acid. The pyrophoric character of the uranium metal powder is decreased by immersing the powder in a solution of about 1.3*M* nickel sulfate. The powder is washed, dried under vacuum, sieved, classified, and stored in an argon atmosphere.

The yield of uranium metal powder in pilot-plant tests has ranged from 95 to 97%. The greatest loss occurred during the filtration and sieving operations. Impurities observed in the powder were 0.5% UN, 0.5% UO_2, and 1 to 3% UH_3. The spontaneous ignition temperature of the powder was observed to be between 110 and 120°C. The average particle diameter was 20 μ with the majority of the particles between 15 and 44 μ in diameter.

Thorium

The present position of thorium in the field of power reactors is in the nature of a reserve material. However, considerable technology on thorium chemistry and metallurgy is already available to meet any future production demands. Prakash et al.[33] have published a review of the current methods for processing thorium ores to metal. Complete details of the metallurgy and fabrication of thorium metal are presented.

Two new process flow sheets have been developed recently by the U. S. Bureau of Mines to recover thorium from thorite ores[34] and monazite concentrates.[35] Both processes utilized a sulfuric acid leach to extract the thorium values from the ore, followed by solvent extraction of the leach solution with a primary amine to yield a product containing 99% thorium oxide.

Production of Thorium Oxide

Dense particles of thorium dioxide, suitable for vibratory compaction into tubes with a bulk density approaching 90% of theoretical, have been prepared at Oak Ridge National Laboratory (ORNL)[36] by a sol-gel process. In the sol-gel process (Fig. V-2), a thorium dioxide hydrosol is carefully evaporated to a gel, from which glassy millimeter-size thorium dioxide particles of 99% theoretical density are produced by calcination to 1150°C.

The thorium dioxide feed for preparing the hydrosol may be produced by denitration of thorium nitrate. Hydrated thorium nitrate crystals are converted to thorium dioxide in a two-step denitration process. In the first step of the process, the crystals are partially denitrated in superheated steam in the temperature range of 180 to 290°C. In the second step the denitration reaction is completed by heating the intermediate product at 320 to 500°C. The nitrogen content of the thorium dioxide product is equivalent to a nitrogen-to-thorium mole ratio of 0.10. Engineering-scale tests on the denitration reaction are being conducted in a 14-in.-diameter rotary calciner.[37,38]

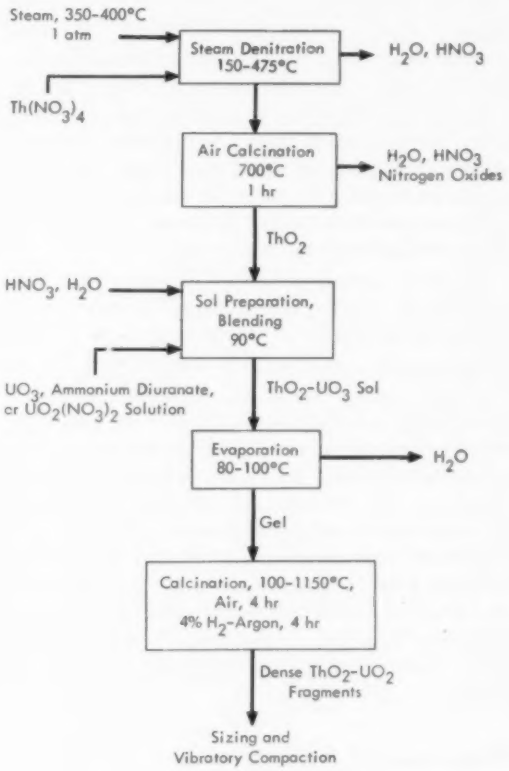

Fig. V-2 Sol-gel process for preparation of dense thorium-uranium oxide.[36]

Thorium dioxide powder is dispersed in water or dilute nitric acid to produce a stable sol 2*M* in thorium. The *p*H of the sol must be maintained between 3 and 4 in order to keep the nitric acid concentration in the peptization range dur-

ing the evaporation step. Up to 10 mole % uranium may be added to the thorium oxide sol as uranium trioxide, ammonium diuranate, or uranyl nitrate solution. If the nitrate is used, the nitrate concentration of the sol must be adjusted to compensate for that added with the uranium. A 2-hr digestion at 90°C after uranium addition appears adequate to ensure a product homogeneous with respect to the uranium-to-thorium ratio. The thoria sol is converted to a glassy gel by careful evaporation, the primary requirement being evaporation without boiling. This has been successfully accomplished by surface evaporation at 80 to 90°C and, in engineering-scale tests, by evaporation in a steam-heated vacuum tray dryer.

Thorium oxide particles of greater than 99% theoretical density are obtained by calcination of the thoria gel in air for 4 hr at 1150°C. The recommended calcination procedure is to raise the temperature of the gel to 1150°C at a rate not exceeding 300°C/hr. If the rate at which the temperature is raised to 300°C/hr is limited, maximum-strength particles are produced with minimum decrepitation. If uranium is present, an additional 4-hr calcination in an argon atmosphere containing 4% hydrogen is required to reduce the uranium oxides to uranium dioxide. Thoria-urania particles (containing 4.4 wt.% uranium) that were prepared by this process had a density of 9.9 as compared with a theoretical density of 10.0.

Preparation of Thorium Metal

A process has been developed at Ames Laboratory[39] for producing thorium metal by the reduction of thorium tetrachloride with magnesium. The thorium tetrachloride employed in the reduction studies was prepared by the chlorination of thorium dioxide with chlorine in the presence of graphite powder. Purification of the tetrachloride was effected by multiple sublimation under reduced pressure.

The reduction tests were performed by heating a mixture of thorium tetrachloride and magnesium in a tantalum crucible for 1 hr at 965°C under an inert-gas atmosphere. Sufficient magnesium was added to the charge to reduce the tetrachloride and to form a thorium–20 wt.% magnesium alloy product. The alloy product was crushed and heated under a prescribed schedule to 920°C *in vacuo* to remove the magnesium and residual slag. A stepwise heating cycle was employed during the magnesium removal step to avoid melting of the alloy. The final thorium sponge was consolidated by nonconsumable arc melting.

Thorium metal produced industrially by bomb reduction or by electrolytic methods contains, apart from metallic impurities, certain nonmetallic impurities that greatly affect the properties of the metal, particularly its hardness. Several methods have been developed to remove nonmetallic impurities from thorium metal. Peterson[40] has found that calcium metal is an effective agent in removing oxygen from thorium. Treatment of thorium with calcium at 1000 to 1200°C made possible a decrease in the oxygen content of the metal to 16 ppm without changing the purity with regard to other elements. This purification treatment can be applied to thorium metal in any convenient form such as rod or sheet which does not have an excessive section thickness. Deoxidation of powder or sponge would be hindered by the increased difficulty of removing the calcium oxide formed. Other methods for reducing nonmetallic impurities which are currently being investigated are iodide refining[41] and electron-beam melting.[39]

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